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A FURTHER STUDY OF THE PRODUCTS FORMED BY THE ACTION OF HEAT ON PARASULPHAMIDOBENZOIC ACID[1]

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In 1894 Hartman, working in this laboratory on the action of heat on *p*-sulphamidobenzoic acid, made, among others, the following observations:[2] (1) When heated to 285° the acid is converted into a compound wholly soluble in water, which he showed to be the acid ammonium salt of *p*-sulphobenzoic acid. (2) When heated to 235° no loss in weight occurs, the products being, however, only partially soluble in water.

In 1895 Muckenfuss,[3] also working in this laboratory, took up the work at this point. From the mass obtained by heating *p*-sulphamidobenzoic acid to 220° for eight hours he isolated the following substances: Free *p*-sulphobenzoic

[1] The experimental investigation, an account of which is given here and in other papers soon to follow, was carried out some years ago under my direction. The publication of the results has been delayed because of the necessity of my withdrawing from laboratory work. The nature of the main reactions involved has recently been made clear by some work done by Dr. C. A. Rouiller, and the older investigations will now published with apologies to the authors for the long delay.—I. REMSEN.

[2] Diss., Johns Hopkins, 1894

[3] THIS JOURNAL, 18, 349.

acid, the acid ammonium salt of *p*-sulphobenzoic acid, an insoluble and infusible substance which he refers to as the "infusible diamide of *p*-sulphobenzoic acid," and an acid which he describes as iso-*p*-sulphamidobenzoic acid.

For the sake of comparing the "infusible diamide" with the ordinary variety, the latter was prepared by the following two methods: (1) *p*-Sulphamidobenzoic acid was converted into the acid ammonium salt by heating with hydrochloric acid in a sealed tube; from this the neutral potassium salt was obtained, which gave the chloride on treatment with phosphorus pentachloride. From the chloride, the diamide was formed in the usual manner. (2) *p*-Sulphamidobenzoic acid was converted into the chloride, which was then treated with ammonia. Both these methods gave the same substance, which crystallizes in needles and melts at 230°. It is soluble in dilute caustic soda, from which solution one atom of nitrogen is given up in the form of ammonia on boiling, the sodium salt of *p*-sulphamidobenzoic acid being formed.

The "infusible diamide" crystallizes in plates, and is soluble in dilute caustic soda. Instead of losing one atom of nitrogen as ammonia on boiling, both are given off, the neutral sodium salt of *p*-sulphobenzoic acid being formed.[1] Both the diamides yield the acid ammonium salt of *p*-sulphobenzoic acid when heated with hydrochloric acid in a sealed tube at 200°.

From the alcoholic extract of the mass resulting from the fusion of *p*-sulphamidobenzoic acid at 220° for eight hours, Muckenfuss obtained flakes of a substance which proved to be an acid. He made and analyzed the barium salt, and found it to contain an acid which he thought was isomeric with *p*-sulphamidobenzoic acid and which he called "iso-*p*-sulphamidobenzoic acid." The barium salt yielded the potassium salt of *p*-hydroxybenzoic acid when heated with concentrated caustic potash.

This was about the condition of affairs when the present work was taken up.

Preparation of Material.—It was at first thought that pos-

[1] THIS JOURNAL, **18**, 356.

sibly the formation of the "infusible diamide" and the "iso acid" might be due to the impurities which are known to exist in *p*-sulphamidobenzoic acid derived from commercial saccharin. An attempt was made to purify the acid from this source by repeated crystallization. Two hundred and twenty grams of the acid obtained from commercial saccharin were subjected to repeated crystallization from hot water. In no case did the crystals come out colorless, but always had a slightly brownish tinge. The crystallization was repeated seven times with the same result. The melting points of the different crystallizations were neither constant nor sharp. They seem to vary with the time taken in heating the melting-point bulb.

After the seventh crystallization it was decided to use the substance synthetically prepared by the method devised by Remsen.[1] As an additional precaution, the crude *p*-sulphamidobenzoic acid, obtained by the oxidation of *p*-toluenesulphonamide, was dissolved in sodium carbonate, the unoxidized amide filtered off and the acid precipitated by hydrochloric acid and finally purified by crystallization from water. Thus prepared, the acid is perfectly white and pure.

Portions of this product, which had been perfectly dried, were heated to 220°, as described by Muckenfuss. The same sublimates appeared, and the molten mass had the same general appearance as stated by him. When the product was treated with water an insoluble substance remained, which was purified by the method devised in the previous work.[2]

Properties of the "Infusible Diamide."—It is infusible and insoluble in alcohol, ether, chloroform, benzene and ligroin. It is slightly soluble in hot water, coming out in glistening plates on cooling. It is not attacked by boiling concentrated hydrochloric acid, and apparently by nitric acid, although it is soluble in this reagent. It is soluble in cold concentrated sulphuric acid, and the solution is not decomposed at 200°. It is not attacked by carbonates in the cold, but sodium car-

[1] Ann. Chem. (Liebig), **178**, 297.
[2] This Journal, **18**, 353.

bonate liberates ammonia on boiling.[1] In all these respects it is identical with the substance obtained by Muckenfuss.

Action of Phosphorus Pentachloride on the "Infusible Diamide."—In the previous work it was stated that there is no reaction between these substances at 200°. It was found that on heating a specimen of the "diamide" with phosphorus pentachloride, *p*-chlorobenzonitrile is formed at 194°–197°. It was identified by its odor, volatility with water vapor, melting point (94°) and the formation of crystals from alcohol and benzene solutions, agreeing in every respect with the compound described by Remsen and Dohme.[2] The reactions may be expressed as follows:

$$p\text{-}C_6H_4\begin{matrix}CO\\SO_2\end{matrix}\!>(NH_2)_2 + PCl_5 = p\text{-}C_6H_4\begin{matrix}CN\\Cl\end{matrix}\!< + NH_4Cl + POCl_3 + SO_2$$

The reaction is very clean, a large yield of the chlorobenzonitrile being obtained.

Action of Hydrochloric Acid on the "Infusible Diamide."—In the former work it was found that sodium hydroxide sets free all the nitrogen of the "diamide" as ammonia, even at 0°. The conclusion drawn was that in the "diamide" both the nitrogen atoms bear the same relation to the molecule. It was thought that by using different agents one of the nitrogen atoms might be removed, leaving the other, and that from a study of the compounds thus formed, something might be deduced as to the structure of the "diamide" itself.

The first attempts were made with hydrochloric acid of varying concentrations and under different pressures.

In the first experiment fifth-normal acid was used at atmospheric pressure. The "diamide" was boiled for several hours, but no change could be detected. Then acid of specific gravity 1.12 was tried under the same conditions. After boiling for several days, a small amount of the acid ammonium salt of *p*-sulphobenzoic acid, together with ammonium chloride, was found in the solution. A second portion was

[1] Page 5.

[2] This Journal, 11, 347.

similarly treated for a week, but the amount of *p*-sulphobenzoic acid, which was recognized by its characteristic acid barium salt, was not appreciably increased. This long-continued boiling with dilute hydrochloric acid renders the crystals of the "diamide" much larger than they were at first.

Another sample was treated with concentrated hydrochloric acid in a closed vessel at 100° without appreciable result. Reference has been made to the heating at 200° in a sealed tube. From these experiments it appears that it is impossible to hydrolyze one amido group with hydrochloric acid.

Attempts to Diazotize the "Infusible Diamide."—A specimen of the "diamide," which was partially in suspension and partially in solution in sulphuric acid, was treated in the cold with a solution of sodium nitrite. Apparently no nitrous acid was consumed. The solution was gradually heated, finally to boiling, fresh portions of the nitrite being added from time to time. The "diamide" crystallized out unchanged on cooling. A similar experiment was made, nitrous fumes being used instead of the nitrite solution. This also failed to attack the diamide. This made it evident that neither of the amido groups could be removed in this way.

Action of Sodium Carbonate on the "Diamide."—The action of bases weaker than caustic soda was next taken up, in the hope that only one of the nitrogen atoms would be liberated. To this end a weighed amount of the "diamide" was placed in a flask containing a solution of the base, the flask connected with a tin-tube condenser, and a current of steam free from ammonia passed through. The distillate was caught in a measured volume of standard acid and the amount of ammonia liberated was determined. In the case of sodium carbonate, the hydrolysis proceeded much more slowly than with sodium hydroxide, but a point was soon reached when more than one-half of the nitrogen had been given off as ammonia. This showed that sodium carbonate would not accomplish the desired end, and the experiment was discontinued. Evidently a still weaker base must be used.

Action of Magnesium Hydroxide.—This was prepared by add-

ing sodium hydroxide to an excess of a solution of magnesium sulphate. Any carbonate present would be thrown down as magnesium carbonate, and the excess of magnesium sulphate present and the sodium sulphate formed, being neutral, would not be expected to interfere with the reaction. A preliminary experiment showed that this was true in the case of magnesium sulphate.

The first experiment gave the following results: Sulphuric acid was standardized by weighing as barium sulphate and by titrating against a standard solution of ammonia, methyl orange being used as an indicator. A solution of sodium hydroxide (from the metal) was then titrated against this acid.

1 cc. acid = 28.124 mg. H_2SO_4 = 2.122 cc. alkali; 1 cc. alkali = 10.82 mg. alkali.

0.1700 gram "diamide" gave the following:

Acid used, 22.43 cc.

Alkali used for excess of acid, 44.57 cc.

Acid used is equivalent to 47.60 cc. alkali.

Alkali equivalent of ammonia liberated, 3.03 cc.

Alkali equivalent to total nitrogen as ammonia, 6.28 cc.

The amount of ammonia liberated is equivalent to one-half of the total nitrogen within the limits of error. The ammonia was distilled over in five portions, coming off fairly rapidly at first, but soon so slowly that one and one-half days were required to complete the operation.

The experiment was repeated with a larger amount of the "diamide," and an attempt was made to isolate the soluble magnesium salt formed. The larger amount of magnesium sulphate and sodium sulphate present prevented this, as all the constituents are either soluble or insoluble in the ordinary solvents. In order to overcome this difficulty, pure magnesium hydroxide was precipitated from an excess of magnesium sulphate by caustic soda and the precipitate washed by decantation until barium chloride indicated that only a trace of sulphates was present.

The "diamide" was treated with this mixture and steam was passed through as before. It was observed that as the reaction proceeded, the magnesium hydroxide went largely into

solution. When the distillate came over neutral the operation was discontinued and the excess of magnesium hydroxide filtered off. On evaporating the clear colorless solution nearly to dryness, diamond-shaped crystals, which, when perfect, were clear and colorless, separated out. They were found to contain magnesium, giving a precipitate with caustic soda. On boiling with concentrated caustic soda, ammonia was liberated, a salt of *p*-sulphobenzoic acid being formed, which was recognized by its characteristic acid barium salt.

On the other hand, sodium carbonate does *not* liberate ammonia on boiling, or at least so slowly that the ammonia cannot be detected in a test-tube experiment. This is not what might be expected, for sodium carbonate liberates *all* the nitrogen from the "diamide" as ammonia.

Properties of the Magnesium Salt.—It is very soluble in hot water, the solution requiring some time to become saturated. From a sufficiently concentrated solution, the salt crystallizes out slowly on cooling. Its solution has a slightly bitter taste.

If hydrochloric acid is added to a concentrated solution of the magnesium salt, *no* precipitate is formed, showing conclusively that it is not a salt of *p*-sulphamidobenzoic acid.

Again, if barium chloride is added to a solution of the salt, no precipitate is formed, showing (1) that no sulphates or sulphites were formed during the decomposition of the "diamide;" and (2) that it is not a salt of the "iso" acid, which would be precipitated in the form of the barium salt. The acid forms soluble silver, lead, mercuric, copper and ferric salts.

Analysis of the Magnesium Salt.—For the purpose of analysis, two specimens were prepared: the first was the product of second crystallization of the material separating out from the solution of the magnesium salt which had been concentrated by evaporation; the second consisted of the crystals which separated on evaporating the combined mother liquors. The crystals of both specimens were well formed. They were dried by allowing to stand on paper in the air, during which time they lost part of their water, becoming opaque.

First specimen:

1.4730 gram lost 0.2144 gram H_2O at 135°.

0.1820 gram gave 0.0178 gram MgO.

Second specimen:

0.6294 gram lost 0.0926 gram H_2O at 135°.

0.2040 gram gave 0.0200 gram MgO.

The salt may be heated to 275° without further loss.

Specimen	H_2O	MgO
I	14.56	9.78
II	14.71	9.86

These figures were sufficient to show the identity of the two specimens, and from this we may infer that this salt is practically the only substance, besides ammonia, formed in the decomposition.

Analyses for sulphur and nitrogen gave the following results:

0.1660 gram gave 0.1858 gram $BaSO_4$.

0.1500 gram gave 0.1652 gram $BaSO_4$.

The nitrogen was determined by treating the salt with a large excess of caustic potash, passing steam through the hot solution and titrating the ammonia liberated.

0.6097 gram gave ammonia equivalent to 10.68 cc. caustic soda solution containing 0.01082 gram NaOH per cc.

0.4621 gram gave ammonia equivalent to 8.27 cc. of the same solution.

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Mg + 4H_2O$	Found I	Found II
H_2O	14.52	14.56	14.71

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Mg$	Found I	II	III	IV	V	VI
Mg	5.66	5.87	5.88	....	....	....	....
N	6.60	....	....	6.63	6.77	....	....
S	15.09	....	....	....	....	15.37	15.11

From these results it is clear that the substance is a salt of an acid isomeric with *p*-sulphamidobenzoic acid, and at the same time entirely different from the compound described as "iso-*p*-sulphamidobenzoic acid" in the former work.

The Potassium Salt.—The potassium salt was next studied. It was made by precipitating the magnesium from the magne-

sium salt by potassium carbonate, a solution of which was added gradually to a solution of the magnesium salt until no more precipitate was formed.

On evaporating to the proper concentration, fine crystals of the potassium salt were formed. These were clear and colorless, and even in the small amount prepared thick crystals, over a cm. long, were formed. The crystal faces were too indistinctly developed to permit of a determination of the crystal form. The potassium salt is very soluble, but not quite so much so as the magnesium salt. The following analytical results were obtained: On heating to 308°, the salt did not lose weight nor show any signs of decomposition.

0.1505 gram gave 0.1468 gram $BaSO_4$.

0.1563 gram gave 0.0574 gram K_2SO_4.

0.2030 gram gave 0.0737 gram K_2SO_4.

0.3496 gram gave ammonia equivalent to 5.56 cc. NaOH solution (1 cc. = 0.01082 gram NaOH).

	Calculated for $C_6H_4 < \begin{matrix} CONH_2 \\ SO_2OK \end{matrix}$	Found I	II	III	IV
K	16.32	16.28	16.46	....	..
S	13.39	....	....	13.43	. ..
N	5.86	....	.....	....	6.02

Action of Phosphorus Pentachloride on the Potassium Salt.—In order to determine whether the infusible "diamide" could be regenerated from the potassium salt, the latter was first treated with phosphorus pentachloride.

Reaction takes place very easily at a temperature slightly above that of the room. When treated with water, the product formed by the pentachloride breaks up into a pulverulent form, no apparent reaction between it and the water taking place. Indeed, it may be boiled with water without going into solution or losing its characteristic appearance. It is comparatively insoluble in the organic solvents with the exception of alcohol, in which it is very soluble and from which it can be crystallized. This solution may be boiled without decomposition. Ammonia dissolves the substance readily with evolution of heat, ammonium chloride being formed dur-

ing the reaction. The extreme solubility of the substance shows that it is *not* the infusible "diamide."

Discussion of Results.—The acid whose salts have just been described is clearly isomeric with *p*-sulphamidobenzoic acid. *p*-Carbamidobenzenesulphonic acid would be such a compound. The fact that phosphorus pentachloride reacts with the potassium salt at a low temperature is certainly not unfavorable to this view. Also the formation of ammonia on boiling with caustic soda indicates this structure, for *p*-sulphamidobenzoic acid, in which the nitrogen is unquestionably in combination with sulphur, does not react in this manner. This would lead to the assumption that in the infusible "diamide" both nitrogen atoms are in combination with carbon. As these are the only facts available, the question as to the constitution of the infusible "diamide" still remains an open one.

The "Iso" Acid

This substance is obtained in flakes from the alcoholic extract of the mass resulting from the fusion of *p*-sulphamidobenzoic acid at 220° for eight hours. On dissolving these flakes in water, making alkaline with ammonia, and adding barium chloride, the characteristic barium salt described by Muckenfuss is obtained. This can be purified by treatment with animal charcoal, boiling for a few minutes and crystallizing. The large amount of charcoal and the long-continued boiling mentioned in the previous work were found to be unnecessary.

Formation of the Acid from the Barium Salt.—The pure barium salt thus obtained was treated with the calculated amount of standard sulphuric acid, the barium sulphate filtered off and the filtrate evaporated, first over a free flame and finally on a water bath. As the solution becomes concentrated, no crystals appear, but as the evaporation approaches completion, the acid forms a thick, gummy skin over the surface of the liquid. The layers deposited on the sides of the dish become lemon-yellow in color when the breath is blown upon them or when they are protected in any way from the water vapor from the bath. This color disappears when the vapors

come in contact with the substance again. This is characteristic of the "iso" acid.

Properties of the "Iso" Acid.—The acid thus prepared is lemon-yellow throughout when dry. It is deliquescent, becoming pasty on standing in the air. On treatment with water it goes easily into solution, the yellow color disappearing as soon as the water comes in contact with it. From a fairly concentrated water solution, alcohol precipitates the acid in very minute crystals which settle in flakes. The solution is acid toward litmus and has a sharp sour taste.

Action of Concentrated Hydrochloric Acid on the "Iso" Acid.—About one-half gram of the "iso" acid was heated with concentrated hydrochloric acid in a sealed tube in a water bath. The "iso" acid dissolved slowly, and there remained an insoluble portion even when the tube was hot. On cooling, more of the same insoluble matter appears, together with clear, colorless crystals of a more soluble compound. These crystals dissolve readily on adding a little water. On evaporating the hydrochloric acid and taking up with water, an insoluble portion remained which has the following properties: (1) It is fairly insoluble in hot water, but crystallizes from water solution in clear, colorless plates. (2) It is infusible within the range of the thermometer (360°). (3) It is soluble in dilute caustic soda and is reprecipitated by hydrochloric acid; it gives off ammonia on boiling with caustic soda. It agrees in all these properties with the infusible "diamide."

During the evaporation mentioned no yellow color appears, nor is the residue yellow, indicating the absence of the "iso" acid.

On evaporating the filtrate from the insoluble matter also, no yellow color appears, although no hydrochloric acid is now present. On treating the residue from this last evaporation with water, a second insoluble substance appeared, which had the same general appearance as the first. It was obtained in too small quantity to permit of thorough investigation.

Effect of Repeated Evaporation on the "Iso" Acid.—A portion of the "iso" acid was repeatedly evaporated with fresh portions of water on a water bath in order to test whether the forma-

tion of the insoluble substance could be accomplished in this way. The evaporation was repeated six times without result.

Action of Water on the "Iso" Acid.—On heating a solution of the "iso" acid in a sealed tube to the temperature of a saturated salt-water bath for several hours, no change was noticed. When a sufficiently concentrated solution is heated in a sealed tube at 220°, crystals separate out on cooling. These are very thin plates which are prolonged in one direction. The amount obtained was too small for an examination.

Action of Dry Air upon the "Iso" Acid.—A specimen of the "iso" acid which had been kept over calcium chloride for several weeks was heated in a current of dry air to 107°.

0.9815 gram gave 0.0893 gram water at this temperature.

	Calculated for $C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} \left[\begin{matrix} OH \\ NH_2 \end{matrix} \right]$	Found
H_2O	8.96	9.10

No further appreciable loss took place up to 175°. After the heating the material was still completely soluble in water. Hence the formation of an insoluble substance is not due to air alone.

Action of Various Gases on the "Iso" Acid

Steam.—A weighed sample of the anhydrous "iso" acid was placed in a porcelain boat in a glass tube running through an asbestos-covered air bath. A slow current of steam was now passed through the tube, which was kept at a temperature of 175°. After replacing the steam by dry air, cooling and weighing, a slight loss was indicated which was not sufficient to account for any deep-seated change. A portion was withdrawn and was found to contain no insoluble matter.

Dry Hydrochloric Acid Gas.—It was thought that possibly this might act as a dehydrating agent. In order to test this, the gas, after passing over the substance, was passed through a weighed U-tube filled with glass beads which had been moistened with concentrated sulphuric acid. It was found that after heating in a current of the gas from 175° to 190°, neither the U-tube nor the substance had changed appreciably in

weight. After the operation the substance was as soluble as before.

Moist Hydrochloric Acid Gas at 125°.—This experiment was performed in the same manner as above, and similar results were obtained, i. e., no insoluble matter was formed, nor was there any change in weight. The same sample of the "iso" acid was used in all these experiments.

The sample which was withdrawn to test the solubility after heating in dry hydrochloric acid gas was evaporated with concentrated hydrochloric acid. No insoluble matter was formed.

Preparation of the Barium Salt.—Four specimens of the barium salt were prepared in order to test the analytical results given in the former work.

I. Made from the water extract of the molten mass by rendering it slightly alkaline with ammonia and precipitating by barium chloride. This was treated with animal charcoal and crystallized twice.

II. The same as above, crystallized a third time.

III. Made from a specimen of the "iso" acid, prepared by treating the barium salt, which had been twice crystallized, with sulphuric acid. The salt obtained in the usual way from this acid was twice crystallized.

IV. Made from the flakes which separate from the alcoholic extract of the molten mass.

All the crystallizations mentioned were from hot water. The specimens were all dried on paper. They were identical in solubility and crystal habit, and all the specimens were white.

Analysis of the Barium Salt.—I. 0.5183 gram lost 0.0526 gram at 100°–110° and 0.0100 gram at 200°–215°.

II. 0.5137 gram lost 0.0537 gram at 100°–110° and 0.0085 gram at 200°–210°.

III. 0.1582 gram lost 0.0193 gram at 200°–210°.

IV. 0.3315 gram lost 0.0350 at 100°–110°, 0.0033 gram at 150° and 0.0053 gram at 200°–220°.

Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Ba$		Calculated for $(C_6H_4<^{CO}_{SO_2}>N)_2Ba$		Specimen	Found	
H_2O	H_2O	H_2O	H_2O		At lower temperature	At higher temperature
+3.0	9.14	+3.0	9.73	I	10.15	12.08
+3.5	10.5	+3.5	11.17	II	10.45	12.11
+4.0	11.82	+4.0	12.56	III	....	12.20
				IV	at 150°	
					10.55	11.55 12.16

The salt dries slowly in the air. A specimen which had been exposed about three weeks lost 1.1 per cent. in weight.

Barium Determinations.—I. Anhydrous salt:

(*a*) 0.2240 gram gave 0.1028 gram $BaSO_4$.

(*b*) 0.2473 gram gave 0.1125 gram $BaSO_4$.

II. (*a*) Anhydrous salt:

0.1546 gram gave 0.0713 gram $BaSO_4$.

(*b*) Hydrous salt:

0.2005 gram gave 0.0821 gram $BaSO_4$.

III. Anhydrous salt:

0.1395 gram gave 0.0643 gram $BaSO_4$.

IV. Hydrous salt:

0.1002 gram gave 0.0410 gram $BaSO_4$.

These results are tabulated below.

Calculated for $(C_6H_4<^{CO}_{SO_2}>N)_2Ba$		Specimen	Found	
Ba	27.34	I	(*a*) 26.97	(*b*) 26.75
		II	(*a*) 27.11	
		III	27.10	
Calculated for $(C_6H_4<^{CO}_{SO_2}>N)_2Ba + 4H_2O$				
		II	(*b*) 24.07	
Ba	23.91	IV	24.06	

The results are sufficient to show that all four specimens are identical.

Sulphur and Nitrogen Determinations.—0.1665 gram gave 0.1570 gram $BaSO_4$ (Liebig).

0.1671 gram gave 0.1564 gram $BaSO_4$.

0.2035 gram gave 10 cc. nitrogen at 24° and 760 mm. (Dumas).

0.2009 gram gave 10 cc. nitrogen at 23° and 748 mm.

	Calculated for $(C_6H_4<^{CO}_{SO_2}>N)_2Ba$	Found I	II	III	IV
S	12.77	12.95	12.89	....	....
N	5.59	...	...	5.49	5.49

Conductivity Determinations

Preparation of Materials.—It was thought desirable to compare normal *p*-sulphamidobenzoic acid with the "iso" acid by means of their electric constants. For this purpose the pure sodium salts of the acids, as well as the acids themselves, are required. The normal acid was prepared as before mentioned.

The sodium salt of the normal acid was prepared by dissolving the acid in a slight excess of sodium hydroxide (from the metal). It was then precipitated by alcohol, filtered, washed with alcohol to neutral reaction, crystallized from a mixture of alcohol and water, again washed with alcohol and finally dried in the air.

Thus prepared, the salt consists of white, micaceous crystals, which are light and bulky. Analysis gave good results for sodium and showed that the salt contained no water of crystallization.

The sodium salt of the "iso" acid was prepared by neutralizing the free acid with caustic soda. On adding a large excess of this, the salt is precipitated. It was filtered, washed to neutral reaction with alcohol, dissolved in water, treated with a small amount of animal charcoal for a few minutes, filtered and precipitated with alcohol, filtered, washed with alcohol and dried in the air.

Thus prepared, the salt consists of a mass of very small white crystals.

The yellow color formed on evaporating a solution of the "iso" acid, which it retains on standing over calcium chloride, is not imparted to the sodium salt but seems to remain in the mother liquor. Animal charcoal does not destroy it in a short time.

Analysis of the Sodium Salt.—0.19005 gram lost 0.0296 gram H_2O at 100°.

0.3465 gram lost 0.0551 gram H_2O at 100°.

0.1622 gram gave 0.0544 gram Na_2SO_4.

0.2813 gram gave 0.0958 gram Na_2SO_4.

Calculated for $C_6H_4<^{CO}_{SO_2}>N.Na + H_2O$		Found I	Found II
H_2O	15.35	15.54	15.90

Calculated for $C_6H_4<^{CO}_{SO_2}>N.Na$		Found I	Found II
Na	11.22	10.86	11.03

The only available method of purifying the "iso" acid is the one which has been mentioned, and this gives a yellow substance.

The conductivity determinations were made by the method devised by Kohlrausch. The cell constants were determined by means of a fiftieth-normal solution of potassium chloride. The temperature was 25°. The results are given in the following tables:

The Sodium Normal Salt

V	First solution μ	Second solution μ	Third solution μ
10	57.41	...	...
20	61.73	...	...
40	64.98	...	...
80	67.33	66.78	...
160	69.64	68.35	...
320	71.62	70.86	...
640	73.45	72.31	70.44
1280	...	...	74.91

The second and third columns give the results obtained by the successive dilution of a tenth- and an eightieth-normal solution, respectively.

The Sodium Salt of the "Iso" Acid[1]

V	First solution	Second solution
9.24	62.72	...
18.48	70.45	...
36.96	75.63	75.63
73.92	80.06	78.96
147.84	84.05	83.55
295.68	86.95	87.32
591.36	89.54	91.61

[1] These solutions were made under the assumption that the "iso" acid was an isomer of *p*-sulphamidobenzoic acid. Afterward the normality was calculated for *p*-benzoic sulphinide. This accounts for the fractions in the V column.

The results are interpolated in the tables below in order that Ostwald's method for calculating the conductivity at infinite dilution of the sodium salts and the acids might be applied.

The Normal Salt

V	μ	Δ	μ_∞ for salt	μ_∞ for acid[1]
32	62.38	12	74.38	350.18
64	66.39	10	76.39	352.19
128	68.71	8	76.71	352.51
256	70.84	6	76.84	352.63
512	72.82	4	76.72	352.52

The "Iso" Salt

32	74.24	12	86.24	362.04
64	78.87	10	88.87	364.67
128	83.0	8	91.0	366.8
256	86.17	6	92.17	367.97
512	88.90	4	92.90	368.7

It will be observed that the conductivities at infinite dilution for both the normal acid and its sodium salt agree for the different dilutions, but that the figures do not agree in the case of the "iso" acid. In the latter case the conductivity increases with the time the solution is subjected to the action of the current, a phenomenon which has been observed in the case of other salts.[2] In order to obviate this error a solution was made and its conductivity determined as soon as possible. This gave a result of 368.64 for the acid, but the value increases rapidly, a very dilute solution showing an increase of 1.82 units in five minutes, and 3.68 units in ten minutes.

The Normal Acid

The normal acid is very slightly soluble at the temperature of the experiment (25°). The solution used contained 0.0350 gram in 500 cc.

V	μ	
2874	224.4	$K = 0.0388$[3]
5748	246.15	$K = 0.0281$

[1] μ_∞ for sodium salt + 275.8 = μ_∞ for acid.

[2] Jones and McKay: THIS JOURNAL, **19**, 105.

[3] $K = \dfrac{(\mu_v/\mu_\infty)^2}{V(1-\mu_v/\mu_\infty)}$.

The "Iso" Acid

Solution contained 0.1343 gram in 25 cc.

V	μ
34.092	323.27
68.184	331.9
136.368	341.43
272.736	359.1
545.472	369.3
1090.944	376.4

If we compare the limiting value of the conductivity of the "iso" acid, as calculated from its sodium salt, with the results obtained by using the acid itself, we see that the latter values exceed the former at a relatively small dilution. This would indicate the formation in solution of simpler molecules having a greater number of ions, and consequently the validity of the results in determining the coefficient of affinity (K) is destroyed.

Action of Hydrochloric Acid on the Barium Salt of the "Iso" Acid.—A small amount of the barium salt was boiled seven hours with dilute hydrochloric acid (sp. gr. 1.12). On standing overnight, crystals separated out which dissolved on heating; on cooling, they again appeared and redissolved without difficulty. On repeating the operation, they all dissolved with the exception of a few particles, which increased in number on boiling until a good yield was obtained.

The substance is crystalline and fairly insoluble; it contains barium, but no nitrogen could be detected on fusion with metallic sodium. The properties of the substance resemble those of acid barium *p*-sulphobenzoate, but the amount obtained was too small to be tested. For the sake of obtaining more of this substance, a larger amount of the barium salt was treated as above. The boiling was continued for eighteen hours and the salt was repeatedly crystallized out and redissolved, but the insoluble substance did not appear. Instead of this, the crystals which are formed on cooling from time to time gradually lose the characteristic silky form of the barium "iso" salt, coming out finally as very thin flakes which, after filtering, have a white micaceous appearance.

The salt gives off ammonia when fused with caustic potash. After recrystallizing, the salt comes out in very thin, clear, colorless plates, which are prolonged in one direction. An analysis gave the following results:

0.2865 gram lost 0.0279 gram H_2O at 100°–120°.

0.0998 gram gave 0.0389 gram $BaSO_4$.

Above 200° there is a second slight loss in weight which is accompanied by the formation of a slight sublimate.

	I	II
Ba	22.92	....
H_2O	...	9.74

This would give 25.39 per cent. barium in the anhydrous salt. The theoretical per cent. of barium in the barium salt of *p*-sulphamidobenzoic acid is 25.51 per cent.

A lack of material and of time prevented a further investigation of these compounds.

CONCLUSION

From the analyses of the sodium and barium salts of the "iso" acid, it appears that the acid is *not* isomeric with *p*-sulphamidobenzoic acid, but corresponds to this less one molecule of water.

The composition and properties of the magnesium and potassium salts of the acid derived from the infusible "diamide" of *p*-sulphobenzoic acid show that both are salts of an acid isomeric with *p*-sulphamidobenzoic acid, or an iso-*p*-sulphamidobenzoic acid in reality. The facts known with regard to these salts indicate, but do not show conclusively, that in the infusible "diamide" both nitrogen atoms are in combination with carbon, and that the acid really isomeric with *p*-sulphamidobenzoic acid is probably *p*-carbamidobenzenesulphonic acid.

If the anhydride formula for Muckenfuss' "iso" acid is accepted, the action of heat upon *p*-sulphamidobenzoic acid may be thus represented:

$$4\ p\text{-}C_6H_4{<}\begin{matrix}COOH\\SO_2NH_2\end{matrix} = C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}(NH_2)_2 + C_6H_4{<}\begin{matrix}COOH\\SO_2OH\end{matrix}$$
$$+ C_6H_4{<}\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NH.$$

It will be remembered that the products actually obtained, and the only ones obtained, by heating the *p*-sulphamidobenzoic acid are those represented in this equation, that is to say, the infusible "diamide," free *p*-sulphobenzoic acid, acid ammonium *p*-sulphobenzoate and the "iso" acid.

[Contributions from the Sheffield Laboratory of Yale University]

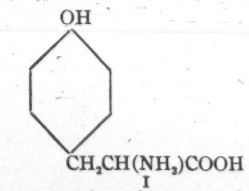
CXCVI.—ON HYDANTOINS

THE ACTION OF BROMINE ON TYROSINEHYDANTOIN

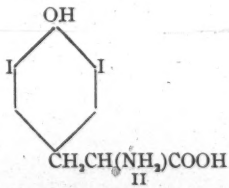
By Treat B. Johnson and Charles Hoffman

[EIGHTH PAPER]

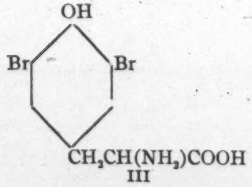
3,5-Diiodotyrosine (iodogorgoic acid) (II)[1] and 3,5-dibromotyrosine (III)[2] can be synthesized easily by the action of iodine and bromine, respectively, on tyrosine (I). Chlorine, on the other hand, does not react smoothly with this amino acid and attempts to prepare the corresponding 3,5-dichlorotyrosine (IV), in this manner, have been unsuccessful.



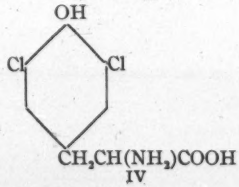
I



II



III

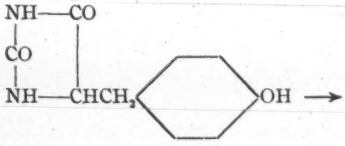


IV

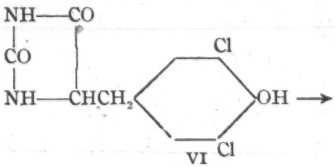
[1] Wheeler and Jamieson: This Journal, **33**, 365 (1905).

[2] von Gorup: Ann. Chem. (Liebig), **135**, 281.

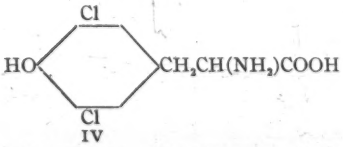
In a recent publication from this laboratory[1] we have described a method for synthesizing easily this interesting amino acid. It was observed, for example, that tyrosinehydantoin (V) is attacked by chlorine, in glacial acetic acid, forming smoothly the hydantoin of 3,5-dichlorotyrosine (VI). When this chloro compound was digested with a strong solution of barium hydroxide it underwent hydrolysis, giving a practically quantitative yield of the dichloroamino acid (IV). We also find that iodine reacts smoothly with tyrosinehydantoin, giving the hydantoin of iodogorgoic acid (VII).



V



VI



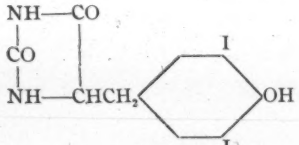
IV

The easy formation of the chlorine- and iodine-substituted hydantoins from tyrosinehydantoin suggested that the corresponding bromohydantoin (VIII) might be prepared in a similar manner.

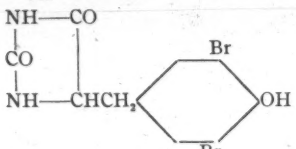
We now find that bromine reacts abnormally with tyrosinehydantoin. While we have been able to show the formation of the corresponding 3,5-dibromotyrosinehydantoin (VIII), nevertheless the chief product of the reaction, in this case,

[1] Wheeler, Hoffman and Johnson: J. Biol. Chem., **10**, 147 (1911).

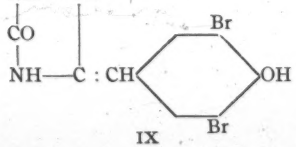
was 3,5-dibromobenzalhydantoin (IX). Therefore this halogen attacks the side chain as well as substitutes in the benzene nucleus. The same 3,5-dibromobenzalhydantoin (IX) was obtained as was formed by the condensation of 3,5-dibromobenzaldehyde[1] with hydantoin. The hydantoin of 3,5-dibromotyrosine (VIII), which can be prepared by the action of potassium cyanate on 3,5-dibromotyrosine (III), or by the reduction of 3,5-dibromobenzalhydantoin (IX) with hydriodic acid, reacted with bromine in glacial acetic acid, giving the original 3,5-dibromobenzalhydantoin (IX):



VII



VIII



IX

Summary

Bromine and iodine react with tyrosine, forming 3,5-dibromo- and 3,5-diiodotyrosines, respectively. 3,5-Dichlorotyrosine is not formed in an analogous manner by the action of chlorine on the amino acid.

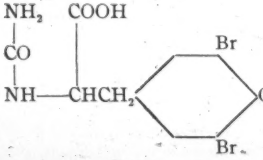
Chlorine and iodine react with tyrosinehydantoin, forming

[1] Paal: Ber. d. chem. Ges., **28**, 2407 (1895).

the corresponding 3,5-dichloro- and 3,5-diiodotyrosinehydantoins, respectively. Bromine reacts abnormally with tyrosinehydantoin, giving 3,5-dibromobenzalhydantoin.

EXPERIMENTAL PART

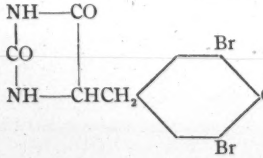
3,5-Dibromo-4-hydroxybenzylhydantoic Acid (*3,5-Dibromotyrosinehydantoic Acid*),



OH.—One gram of 3,5-dibromotyrosine[1] and 0.3 gram of potassium cyanate were dissolved in 50 cc. of water and the solution heated for about fifteen minutes at 100°. The solution was then cooled and acidified with hydrochloric acid, when this hydantoic acid separated. The yield was 1.1 grams. This acid is very soluble in alcohol and fairly soluble in hot water. It crystallizes from alcohol in rhombohedral plates which have a tendency to associate in twins. The acid separates from water in square blocks or prisms which melt at 191° with decomposition. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}O_4N_2Br_2$	Found
N	7.33	7.39

3,5-Dibromotyrosinehydantoin,



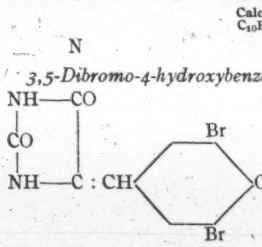
OH.—This hydantoin is formed smoothly by digestion of the preceding hydantoic acid with concentrated hydrochloric acid. The compound is soluble in alkali and is precipitated unaltered by addition of acetic acid. It is difficultly soluble in boiling

[1] von Gorup: *Loc. cit.*

water, moderately soluble in benzene and acetone and very soluble in glacial acetic acid. It crystallizes from 95 per cent. alcohol in diamond-shaped prisms or rhombohedral tables which melt at 223°–225° with decomposition. It was dried for analysis (Kjeldahl) at 120°:

	Calculated for $C_{10}H_5O_3N_2Br_2$	Found
N	7.69	7.52

3,5-Dibromo-4-hydroxybenzalhydantoin,



OH.—Six and seven-tenths grams of 3,5-dibromo-4-hydroxybenzaldehyde,[1] 5.0 grams of hydantoin and 15.0 grams of fused sodium acetate were dissolved in 30 cc. of glacial acetic acid and the solution boiled for 1.5 hours. The solution gradually became dark and after one hour's heating the hydantoin began to deposit. The mixture was diluted with water, when the hydantoin separated. It crystallized from glacial acetic acid in minute, brownish yellow needles which melted above 295° with decomposition. The yield of pure crystallized material was 2.6 grams. The compound is difficultly soluble in alcohol, benzene, acetone and water. It dissolves in alkali, giving a yellow solution, and forms a difficultly soluble yellow ammonium salt. Analysis (Kjeldahl):

	Calculated for $C_{10}H_6O_3N_2Br_2$	Found
N	7.73	7.74

Formation of 3,5-Dibromotyrosinehydantoin by Reduction of 3,5-Dibromo-4-hydroxybenzalhydantoin with Hydriodic Acid

Two and six-tenths grams of the benzalhydantoin were suspended in a mixture of 25 cc. of glacial acetic acid and 15 cc. of hydriodic acid, and the mixture was boiled until the hydantoin completely dissolved. The solution assumed a dark

[1] Paal: *Loc. cit.*

color, due to the separation of iodine. After evaporating to remove the greater proportion of the acetic acid, and then washing with sulphur dioxide water to remove iodine, the 3,5-dibromotyrosinehydantoin deposited. The yield was 1.8 grams. It crystallizes from alcohol in prisms which melt at 223° with decomposition. A mixture of this reduction product and the hydantoin of 3,5-dibromotyrosine melted at exactly the same temperature. The bromine atoms in the dibromobenzalhydantoin therefore are not displaced by hydrogen by reduction with hydriodic acid.

The Action of Bromine on Tyrosinehydantoin.—Two molecular proportions of bromine (6.5 grams) were dissolved in 40 cc. of glacial acetic acid and 4.0 grams of tyrosinehydantoin were suspended in the solution. There was no immediate evidence of a reaction. The mixture was then heated at 100° for one hour, when a crystalline substance had separated from the hot acid solution. This was filtered off and the filtrate saved (see below). The weight of crude, dried material was 3.5 grams. The substance crystallized from glacial acetic acid in needles which melted above 295° with decomposition. It was identified as 3,5-dibromo-4-hydroxybenzalhydantoin. A mixture of the hydantoin with this substance melted at the same temperature. Also when some of the compound was digested in acetic acid with hydriodic acid, iodine was liberated and 3,5-dibromotyrosinehydantoin was obtained. It melted at 223° and also at this same temperature when mixed with some of the pure hydantoin prepared from 3,5-dibromotyrosine.

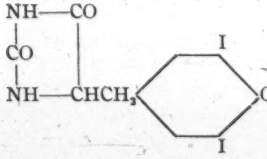
The filtrate (above) was evaporated to dryness, when we obtained 0.3 gram of a crystalline residue which melted at 215°–260°. This was triturated with boiling water, when some unaltered tyrosinehydantoim was dissolved. The insoluble residue was then dissolved in alcohol and the solution cooled, when the 3,5-dibromo-4-hydroxybenzalhydantoin separated in needles melting above 295°. On concentrating the solution further and cooling again, we obtained a crop of rhombohedral prisms. This product was identified as 3,5-dibromotyrosinehydantoin and melted at 222°–223°.

In a second experiment 5.3 grams of bromine (2 mols.) were dissolved in 40 cc. of glacial acetic acid and then 3.4 grams of tyrosinehydantoin were dissolved in the cold solution. The mixture was then allowed to stand at ordinary temperature for about 12 hours. Hydrobromic acid was slowly evolved and the bromine color finally disappeared. The dibromobenzalhydantoin separated under these conditions as a light gray powder. It crystallized from glacial acetic acid and melted with decomposition when heated above 295°. Analysis (Kjeldahl):

	Calculated for $C_{10}H_8O_3N_2Br_2$	Found
N	7.73	7.70

Action of Bromine on 3,5-Dibromotyrosinehydantoin.—One and seven-tenths grams of 3,5-dibromotyrosinehydantoin and 0.8 gram of bromine (one molecular proportion) were dissolved in 20 cc. of glacial acetic acid and the solution heated at 100° for one hour. The bromine disappeared and hydrobromic acid was formed. We obtained a crystalline product, difficultly soluble in the acid, which was identified as 3,5-dibromo-4-hydroxybenzalhydantoin. It crystallized from glacial acetic acid in needles which melted above 295° with decomposition. A mixture of this substance and some of the pure hydantoin melted at the same temperature.

3,5-Diiodotyrosinehydantoin,



.—Three grams of tyrosinehydantoin and 2.5 grams (3 mols.) of potassium hydroxide were dissolved in 50 cc. of water. The solution was cooled to 0°–10° and two molecular proportions of finely pulverized iodine (7.5 grams) were added slowly with vigorous agitation. A small amount of insoluble tarry substance was formed, which we finally separated by filtration.

On acidifying the solution finally with acetic acid 5.7 grams of the iodohydantoin deposited. This corresponds to a yield of 86 per cent. of the calculated. The hydantoin is difficultly soluble in water and moderately soluble in alcohol. It crystallizes from alcohol in hexagonal plates which melt at 235° with decomposition and evolution of iodine vapors. Analysis (Kjeldahl):

	Calculated for $C_{10}H_8O_3N_2I_2$	Found
N	6.11	6.12

NEW HAVEN, CONN.
October 25, 1911

THE ABSORPTION SPECTRA OF COMPARATIVELY RARE SALTS. THE SPECTROPHOTOGRAPHY OF CERTAIN CHEMICAL REACTIONS, AND THE EFFECT OF HIGH TEMPERATURE ON THE ABSORPTION SPECTRA OF NONAQUEOUS SOLUTIONS

BY HARRY C. JONES AND W. W. STRONG

[THIRTY-FIFTH COMMUNICATION]

(*This investigation was carried out with the aid of Grants generously awarded by the Carnegie Institution of Washington.*)

The work discussed in this paper is a continuation of that which has been in progress here during the past five years, and which has been published in part in THIS JOURNAL[1] and in full by the Carnegie Institution of Washington.[2]

The attempt has been made in this work to solve three problems:

First. To map out the absorption spectra of certain comparatively rare substances. Urbain generously forwarded to Dr. Strong ample quantities of the oxides of gadolinium, dysprosium and samarium with which to prepare their salts and study their spectra. We find that the salts of dysprosium

[1] Jones and Uhler: THIS JOURNAL, **37**, 126 (1907). Jones and Anderson: *Ibid.*, **41**, 163 (1909). Jones and Strong: *Ibid.*, **43**, 37 (1910). Jones and Strong: *Ibid.*, **45**, 1 (1911).

[2] Publications of the Carnegie Institution of Washington, Nos. 60, 110, 130 and 160.

and samarium have spectra that are almost as interesting as those of neodymium, with very sharp, characteristic bands.

Second. Under the spectrophotography of chemical reactions we have studied especially the effect of oxidizing agents on uranous salts. We have used milder oxidizing agents and stronger oxidizing agents, and have dissolved the uranous salt in single solvents and in mixed solvents. When uranous chloride is dissolved in a mixture of alcohol and water, both the "alcohol" and the "water" bands come out simultaneously on the plate. A mild oxidizing agent was found to oxidize the "hydrated" salts and to leave unaffected the "alcoholated" salts. A strong oxidizing agent, on the other hand, oxidized both the "hydrated" and the "alcoholated" uranous salt to the uranyl condition. The former is, therefore, an example of "selective oxidation."

Third. By means of the closed cell we have been able to study the absorption spectra of solutions in methyl and ethyl alcohols up to temperatures as high as 195°. The absorption bands widen with rise in temperature up to the highest temperatures employed. Colored solutions, therefore, become more and more nearly opaque as the temperature to which the solutions are subjected is raised.

The effect of rise in temperature on the absorption spectra of neodymium salts in mixtures of alcohol and water, where both the "alcohol" and the "water" bands appear simultaneously, has been studied. The "water" bands are more affected by rise in temperature than the "alcohol" bands, showing that the "hydrates" are less stable with rise in temperature than the "alcoholates."

EXPERIMENTAL METHODS AND APPARATUS

In this work the mapping of the spectra was done in the same way and by the same methods as already described in Publication No. 130 of the Carnegie Institution of Washington, pages 19–22. The general arrangement of apparatus is given in Fig. II.

New difficulties that required special treatment quite frequently presented themselves in the work. As an example,

we might take that of mapping the absorption spectrum of solutions of samarium, dysprosium and gadolinium salts, very kindly lent Dr. Strong by Professor Urbain. In order to bring out as many bands as possible, the absorption cell was made wedge-shaped, the apex of the wedge being about 2 mm. wide and about 15 mm. long. In this way a much greater cell depth could be obtained with the same amount of solution than with the Uhler cell. Another difficulty consisted in getting the strip of the photographic film uniformly exposed. The appearance of bubbles, of precipitates, etc., during the heating of the solutions are further examples. In some cases these difficulties could be overcome. For instance, if the Uhler cell was moved back and forth in the path of the beam of light, bubbles and precipitates only decreased the amount of light passing through the solution and did not cause an uneven exposure on the strip.

Part of the work consisted in extending the Beer's law tests to very dilute solutions. Some work was done on uranyl solutions, a trough with plane parallel ends being used. Other cells consisted of glass tubes with quartz lenses at the ends. One of these was 500 cm. long. With cells of this kind it is impossible to obtain a uniform exposure unless the cell is moved back and forth in the path of the beam of light.

Salt solutions that have bands in the violet and ultraviolet were exposed for much longer intervals of time than those which have bands only in the visible part of the spectrum. In making an exposure of this kind (the uranyl salts are typical examples) the length of exposure to the shorter wave lengths would be from 5 to 10 times longer than to the longer wave lengths. First, an exposure would be made to the whole spectrum of the Nernst glower; then a screen would be placed in front of the plate, cutting out all light of wave length greater than about λ 4500 or λ 4800. A long exposure would then be made to the short wave-length spectrum of the glower; and lastly, a short exposure would be made directly to the spark.

For high-temperature work on acid solutions the fused silica

cell was used, while for room temperatures this cell and the Uhler cell were used for such solutions.

Part of this investigation consisted in extending the work on absorption spectra to high temperatures by means of closed cells. Two cells, one 1.0 cm. and the other 10 cm. in length, were used. Fig. I represents a longitudinal section of the longer cell. Since both cells were exactly alike in all respects except in length and in the size of the side tube, only the longer cell is described here.

The main part of the cell (*I*) was made of tool steel, and was heavily copper plated and gold plated on all the inner surfaces. The side tube was very tightly fitted into the main part of the horizontal tube. The open part of the tube was 1.0 cm. in diameter. The windows of the cell (*U*, *U*) were 2.5 cm. in diameter and were either of quartz or glass. One of the troubles with this form of cell is the formation of precipitates on the inside surfaces of the windows. Every time a precipitate is formed the windows have to be taken out and cleaned. On being put back there is always great danger of the quartz or glass ends being broken. During the work a number of ends were broken in this way.

Quartz ends are much tougher and less easily broken than glass ends. They are, however, quite expensive and in most of the work the solutions were not transparent in the ultraviolet. For this work glass ends were used. Some of these were cut out of ordinary plate glass, and others were made from "uviole" glass, which is tougher and much more transparent in the ultraviolet than is the ordinary plate glass. For cutting the ends a steel tube 2.5 cm. in diameter was fastened to the axle of an ordinary fan motor in such a way that the tube was vertical, the free end of the steel tube being at the bottom. An old glass end was then cemented to a piece of plate glass with hot sealing wax and served as a guide for the steel tube. The plate glass was then held against the end of the steel tube and the motor started. Wet carborundum was fed constantly against the grinding steel tubes. Plates nearly 1.0 cm. thick could be cut in this way in 20 or 30 minutes.

The quartz windows rested on gold washers which, in turn,

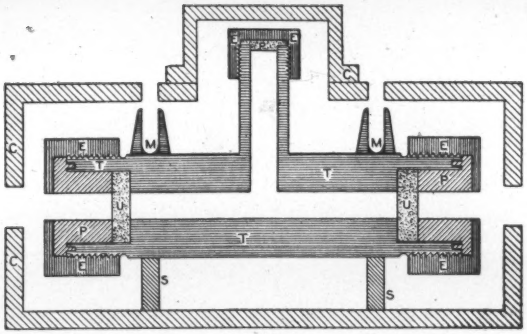


Fig. I

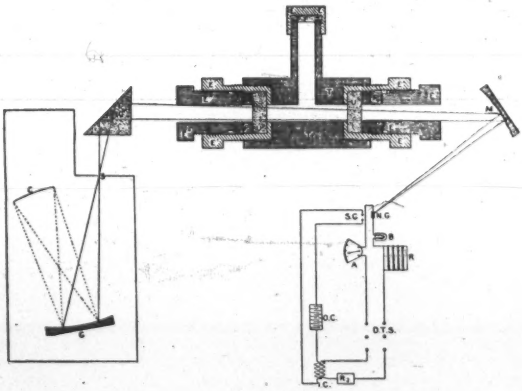


Fig. II.

rested directly against the gold-plated shoulders of the tube T. $P\ P\ P$ are plungers. Two of these at the ends of the main tube have guide pins that prevent them from turning. Between the plungers and the windows were placed washers. Various kinds of washers of hard leather, lead, zinc, etc., were used. The leather washers, however, seemed to be the most satisfactory. Steel caps, $E\ E\ E$, serve to tighten the plungers. $M\ M$ are receptacles for thermometers. C is an iron air bath and prevents rapid changes in temperature in the cells.

In heating a cell of this kind it was found that the rise in temperature must be very gradual. Very great difficulty was encountered in getting the ends to hold liquid-tight. The screw ends were tightened gradually for several days and for several heatings. On one occasion, when the tube was filled with one of the higher alcohols, a very effective closing was made. It is possible that dried films of oils (like linseed oil) might be of use as washers.

In beginning the work no serious trouble from the formation of precipitates was anticipated. This difficulty was encountered, and a new form of cell is being made which it is hoped will overcome some of the imperfections of the form above described. In this form (Fig. II) the quartz ends are fastened in the end E' in the same way as in Fig. I. Instead of the plunger P having guide pins it has guide grooves. Part of the plunger has screw threads, by means of which it can be taken out. The whole cap can be removed from the tube T by unscrewing E', during which the quartz end is untouched. When the ends are removed the quartz window can easily be cleaned. Gold washers are required here between T and E' and between E' and U.

The remaining parts of Fig. II show the arrangement of the apparatus. Only the cell is drawn to scale. The cell is kept in a horizontal position so that all bubbles that form rise in the side tube. As the spectroscope (containing the grating G, photographic plate holder C, and slit S) was kept in a vertical position, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam, the beam being totally reflected by the hypothenuse surface of Q. The

source of light *N. G.* (Nernst glower) or *S. G.* (spark gap) was focused by the concave speculum mirror *M* on the slit *S*. A similar arrangement was used with the fused silica cell. *D. T. S.* represents a double throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current (read by the ammeter *A*) in the Nernst glower may be kept constant.

O C is an oil condenser. Some trouble was given by the condensers, especially when a large spark gap (2 or more cm.) was used for several hours. Paraffin condensers often become heated so that the paraffin melts. A condenser was made of transformer oil. Unfortunately, the box part was made of wood, and it is very difficult to prevent the leaking of the oil from such a box, expecially when it becomes heated. *I C* is an X-ray induction coil and R_2 is a resistance in the primary circuit of this coil.

Some preliminary tests were made with the cells at high pressure. The Cailletet pump belonging to the University was used for this purpose, the cell represented in Fig. I being made so as to fit onto this pump. It was not at all difficult to obtain pressures of 200 atmospheres with water and alcohol solutions. Spectrograms were made of the absorption spectra of neodymium solutions under pressures as high as 275 atmospheres. *No effect of pressure was detected.* The work at high pressures is easier than at high temperatures, on account of the fact that there is an expansion of the cell due to heating.

THE ABSORPTION SPECTRA OF CERTAIN COMPARATIVELY RARE SUBSTANCES

An accurate knowledge of the absorbing power of solutions is the first requisite in understanding the nature of absorption, and, accordingly, the mapping of the spectrum is the first thing to be done. This has been accomplished for a large number of solutions, but there are quite a few salts that have thus far been omitted, and it is the purpose of this chapter to give the results with some of these solutions. This has been

made possible largely through the kindness of Professor Urbain, who loaned Dr. Strong the oxides of samarium, dysprosium and gadolinium. Dr. Guy converted these oxides into the various salts, such as the chloride, nitrate, etc., and dissolved these in various solvents. The other salts whose absorption spectra have been investigated were obtained, for the most part, from Kahlbaum.

Jones and Anderson have shown that the absorption bands of a given salt in any solvent were characteristic of that solvent. For this reason the photographing of the absorption spectra of a given salt in different solvents will be considered as the mapping of characteristic spectra. On the other hand, when a salt is gradually changed to another salt by the addition of an acid to the solution, or by the addition of a foreign salt, the absorption bands show *gradual changes*. This has been interpreted as being due to changes in the molecular aggregates of the salts, and to the formation of intermediate compounds. These changes are considered as being of a chemical nature, and will, therefore, be taken up in the chapter dealing with the spectrophotography of chemical reactions. The facts there described are regarded as furnishing strong evidence for the existence of molecular clustering in liquids, and also for the theory that the absorption and emission centers of spectrum bands consist of more or less complex atomic or molecular aggregates, probably in a process of ionization. The full development of this view appears in the summary.

The experimental methods are essentially those described in Publication 130 of the Carnegie Institution of Washington, and in the chapter on experimental methods in this paper. Nothing more need be said here, except that it would probably be desirable in some cases to place the negative film of an absorption spectrum just below the photographic film that is being exposed. Then, by lengthening the time of exposure very greatly, it should be possible to get a spectrogram containing a great many bands.

The Absorption of Certain Cyanides and Chromates

The early workers on absorption spectra supposed that if

two salts, dissolved in the same solvent, had absorption bands that were close together, the wave lengths of the bands would be modified by the salts being together in the solution. Experiments of this kind have been made without much success. According to the theory of aggregates, however, it would not be expected that any very marked effect would result, unless the two salts formed parts of the same aggregate, the term aggregate being used in the broader sense here to include also molecules of the solvent. Accordingly, the list of colored chemical compounds was searched for salts that contained colored anions and colored cations. An effort was also made to obtain solvents and salts that had bands in the same part of the spectrum. Thus far no good examples have been found where the same spectral aggregates contain different absorbing centers that possess bands in the same region of the spectrum. It seems quite possible, however, that aggregates of this kind among organic compounds may be found, or that in the infrared region many examples of this kind will be discovered. The region of the infrared is especially inviting for work of this kind, inasmuch as nearly all groups possess bands in this region, and the absorbers seem to be of molecular dimensions; whereas in the visible portion of the spectrum it seems probable that, in most cases at least, the constitution of the spectral aggregate influences the period only of vibrators that seem to be of the nature of electrons.

It has been shown that the presence of calcium or aluminium chloride has a considerable influence upon the wave lengths of the uranyl chloride bands. This has been explained[1] as being due to the presence of chlorine, rather than to the direct presence of the calcium or aluminium atoms. It is possible to obtain aqueous solutions of calcium ferricyanide or of aluminium and calcium chromate. If the change of wave lengths of the uranyl bands is not due to calcium and aluminium, then the absorption of the potassium, aluminiun and calcium ferricyanides and chromates should be the same. These salts were studied to test whether or not this was the case.

The dissociation[2] of the ferricyanides, ferrocyanides and

[1] Physik. Z., **11**, 668 (1910).

[2] Publication **130**, Carnegie Institution of Washington, pp. 28 and 29.

chromates is an interesting one, and the study of the absorption spectra of solutions of these salts, especially in the infrared, will probably throw much light upon this subject, but in this work time did not permit us to take up this problem.

Calcium Ferrocyanide and Calcium Ferricyanide.—For cd = 0.74[1] the edge of the absorption band is at about λ 4700. In the case of potassium ferricyanide[2] for a value of cd of 0.69 the edge of the absorption band comes at about λ 4690, the limit of absorption being considered as at λ 4710 and the distance between the limit and the space where the absorption is 50 per cent. as 20 Angström units. It is thus seen that the absorption of calcium ferricyanide is approximately the same as that of potassium ferricyanide. The conclusion follows that calcium shows no bathochromous effect in this instance.

The Chromate and Bichromate of Lithium.—In the case of lithium chromate a change in cd of 0.75 to 6.0 produces an increase in width of the absorption of over 200 Angström units, the edge of the band being at about λ 4850 for cd = 0.75. This is approximately the position of the edge of the absorption band of potassium chromate for a corresponding value of Cd. For lithium bichromate, the edge of the absorption for strip 1, cd = 0.75, is about λ 5350. The values of cd here are much larger, and the absorption is, therefore, much greater than in the case of potassium bichromate previously investigated.

Aluminium and Calcium Chromates.—For corresponding values of cd it seems that the absorption of calcium chromate is less than the absorption of lithium or potassium chromate, and that the presence of calcium does not increase the width of the absorption bands.

Potassium Nickel Chromate and Copper Bichromate.—The absorption of these two salts is an example of the absorption of salts in which both the anion and the cation are colored. The absorption of salts having both ions colored does not seem to be at all different from what we would expect if the

[1] c is the concentration of the solution in terms of normal, and d the depth of the cell in mm.

[2] Publication **130**, Carnegie Institution of Washington, 29.

absorption were additive. Of course, these experiments are very largely qualitative, and it is expected that a rigorous examination along quantitative lines will be made with the radiomicrometer. The above salts are not at all well suited for photographic methods since the limits of absorption and transmission are very large and ill defined.

The Absorption of Solutions of Certain Erbium Salts.—On account of the slight solubility of erbium chloride in the higher alcohols and other organic solvents, very few solutions could be made of sufficient concentration to show the erbium absorption bands. Several of these will be taken up under the effect of change in temperature on absorption spectra.

Hoffmann and Kirmreuther[1] have examined the absorption spectra of certain salts of erbium, using the reflection method, and find a very marked similarity between the spectra of all of the salts investigated, although these may be as different as the chloride and sulphide of erbium. For this reason they conclude that the erbium bands are due to locked electrons and not to saturated valency electrons.

The Absorption Spectrum of Solutions of Certain Neodymium Salts

Previous work has shown us that neodymium and uranous salts show characteristic solvent spectra better than any other colored salts. On account of the sharpness of the neodymium bands, neodymium salts have been made the object of especial study for the existence of solvent spectra. In many cases it is known how the neodymium bands break up in a magnetic field, and it is probably true in general that the absorption of salts of this element has been studied more than that of any of the others. It seems, therefore, probable that ultimately some knowledge of the forces within the solvate may be gained, when it is found how the various neodymium bands are broken up for the different kinds of solvates. In the following pages considerable emphasis will be laid upon the finer structure of the neodymium bands in solutions in the various solvents. A large field of investigation is open for the study of the differ-

[1] Z. physik. Chem., **71**, 312 (1910).

ence in the structure of these bands in solids and especially in crystals. Only a few examples of the latter kind will be described here.

In the description of the groups of neodymium absorption bands, the following nomenclature will be used. This is done for the reason that each one of these groups of bands possesses a characteristic structure for the various solvents, and very often for different salts in the same solvent. While the groups of bands do not change greatly in relative intensities, the finer bands in each group show most extraordinary changes of this kind. The α group includes bands in the region λ 3400 to λ 3600; the β group the bands at about λ 4300; the γ group from λ 4600 to λ 4800; the δ group from λ 5000 to λ 5400; the ε group in the region λ 5800; and the ζ group at λ 6300. In the general discussion of results these groups will be compared under various conditions of temperature, solvent, acid, etc.

In the measurements of the wave lengths of the neodymium bands, the standard spark lines were photographed only in the ultraviolet, so that the measurements of the long wave-length bands here given are not claimed to be very accurate, and are made largely for comparison. On the other hand, the difference in wave length of bands in the same group is much more accurate.

In designating the groups of bands of the neodymium spectra, previous workers started with the red end of the spectrum. This, however, is an unnatural method of procedure when a grating is used, since the spectrograms are all printed with the short wave lengths on the left side and the wave lengths increasing linearly as we pass towards the right. Moreover, it is very doubtful if the ultraviolet absorption spectra of neodymium can be investigated much farther in this region, so that this is the natural end of the spectrum from which to begin naming the groups of bands. On the other hand, it is very probable that there are many more neodymium bands in the infrared, and if these occur in groups, these groups can then be named in their proper order. The reason that the uranyl series of absorption bands was named in the opposite

direction was that the strongest of these bands are at the red end of the series, while the weak bands are in the ultraviolet, the weaker ones of the series in many cases still remaining to be photographed.

Neodymium Chloride in Water.—Some of the weak and fine bands of neodymium and uranium are extremely difficult to obtain clearly on a photographic plate, and it has sometimes seemed to us that the presence of absorption bands of some wave lengths might be due to some absorber that was not always present in the solution. For instance, the presence or absence of foreign nuclei might be a determining factor in the constitution of the aggregates. It might also be possible that aggregates in solution are quite stable as far as their inner constitution is concerned, so that an aqueous solution of neodymium chloride, for instance, might show different absorption bands, depending upon what the species of neodymium chloride aggregates was before the salt was dissolved. It might be possible to detect phenomena of this kind. It would also be very interesting to find whether there is any relation between the kinds of special aggregates of a salt in solution, and the ionic and nucleating centers produced by spraying or bubbling the solution. Nuclei of various salts have been investigated in this manner by Broglie and others. The spray from solutions of the same salt in two or more solvents could be taken up. Samarium and uranous salts could be studied in the same manner.

Plate XXIII, *B*, in the original film, shows bands at $\lambda\lambda$ 4000, 4180, 4271, 4280, 4295, 4330, 4650, 4695, 4805, 5330, etc. So far as we remember, this is the first plate of an aqueous solution on which the very narrow and faint band at λ 4280 has clearly appeared. The band λ 4805 is also a very weak one. In the first strip of the original film, the band λ 4271 possessed very sharp edges and was about 8 Angström units in width. The band λ 4280 was very weak and was not more than 1.5 or 2 Angström units wide. The band λ 4295, on the other hand, was about 8 Angström units wide and very weak. The band λ 4650 is very weak and is seldom seen.

An attempt will be made to compare in as much detail as

possible the bands at λ 4280, λ 5200 and λ 5800 for the various solvents, since it is these bands that give evidences of the existence of solvates and the various aggregates.

Neodymium Chloride as a Methyl Alcoholate.—A solution of neodymium chloride in methyl alcohol that had been allowed to stand over the summer was found to contain a gelatinous precipitate. The absorption spectrum was found to show the neodymium bands quite sharply, these bands having a somewhat different appearance from those in an ordinary methyl alcohol solution.

A sharp band appears at λ 4270, a weaker band about 8 Angström units wide at λ 4295, a wide weak band at λ 3440, the triplets at $\lambda\lambda$ 4700, 4760 and 4830, a very weak band at λ 5100, a wide hazy band at λ 5140, two strong, sharp bands at λ 5220 and λ 5235, a weak and wide band at λ 5260, and bands more or less blurred together at $\lambda\lambda$ 5704, 5780, 5815 and 5860. It will be noticed that the bands at λ 4270 and λ 4295 are relatively stronger than usual. The appearance of these two bands suggests that the precipitate is largely the hydrate of neodymium chloride, the band λ 4270 being a water band and the band λ 4295 an alcohol band.

Neodymium Chloride in Propyl Alcohol.—The α group is composed of the following bands: λ 3445, a rather sharp band about 4 Angstrŏm units in width; λ 3460, about 10 Angström units in width; λ 3490, of about the same intensity and width as λ 3460; λ 3510, very weak; λ 3525, about 4 Angström units wide and quite strong; λ 3540, quite strong and narrow, this band almost running into the more diffuse band at λ 3560; a very weak band appears at about λ 3580. The β group is quite characteristic of the solvent, consisting of a very weak band at about λ 4270, a band at λ 4285 about 10 Angström units wide, and a much wider and weak band at about λ 4330; a wide and weak band appears at λ 4450. The γ group consists of a very weak and diffuse band at λ 4600, and other bands at λ 4700, λ 4770 and λ 4830. The δ group consists of two wide and diffuse bands at λ 5130 and λ 5180, the latter being very weak, and finer bands at λ 5220, λ 5230, λ 5250, λ 5290 and a very weak band at λ 5330. The ε group

consists of the four bands λ 5740, λ 5780, λ 5710 and λ 5850, all being of about the same width, the latter two being considerably the stronger. There are other bands in the red region, but only λ 6880 is at all strong.

Neodymium Chloride in Isopropyl Alcohol.—*A*, Plate I, shows the absorption spectrum of neodymium chloride in isopropyl alcohol. The finer structure of the different groups of bands is quite different from that of the propyl alcohol spectrum.

The α group of this alcohol is very simple, showing only three hazy bands, at λ 3460, λ 3510 and λ 3535, the middle band being much the weaker. Only a single band of the β group shows at λ 265. Other bands appear at λ 4420, λ 4600 (very diffuse), λ 4690 and λ 4730.

The δ group consists of λ 5100 and λ 5320. These bands are quite wide and diffuse. On account of the plate not being properly developed, the bands do not show as much detail as they probably would under more favorable conditions. Even this plate shows the finer bands slightly.

The ε group consists of a broad diffuse band at λ 5720 and two much stronger bands at λ 5780 and λ 5810.

Neodymium Chloride in Butyl Alcohol.—Starting with the ultraviolet, we have λ 3450 very sharp and narrow, λ 3460 weak, λ 3492 somewhat diffuse, λ 3535 very sharp and narrow, λ 3545, λ 3560 very diffuse. The bands $\lambda\lambda$ 4265, 4285 and 4300 are weak and of approximately the same intensity, the band λ 4265 being slightly narrower than the other two. These bands not only differ in relative intensity from the water bands but also in wave lengths, band λ 4265 being of shorter and band λ 4330 of greater wave length than the water bands.

The other bands are quite diffuse and appear at $\lambda\lambda$ 5085 (narrow), 5095 (narrow and very weak), 5130, 5200, 5215, 5240, 5270, 5300, 5710, 5750, 5780, 5820, 5860, 5900 and 5930.

This spectrum is described in detail in the chapter at the end of the monograph. It may be noticed that for the solution of greatest length, the absorption in the ultraviolet is very strong, extending to λ 4100. This is probably due to the

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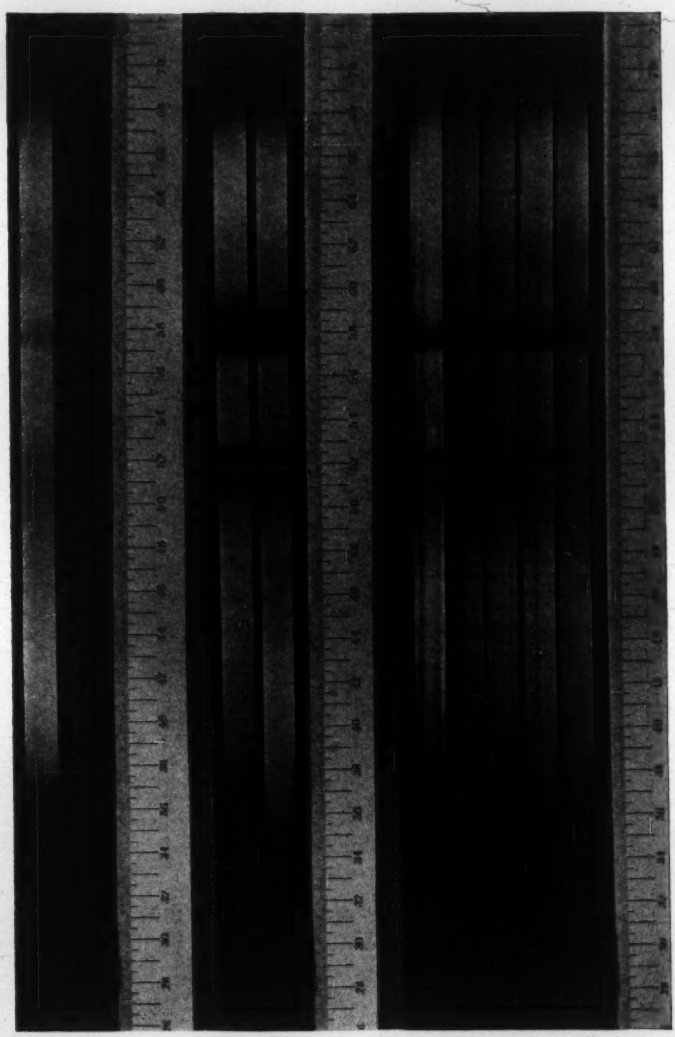
Plate I



propyl alcohol. It is certainly not due to the absorption of the neodymium chloride itself.

Neodymium Chloride in Isobutyl Alcohol.—It will be seen from the wave lengths given below that there are quite marked differences between the absorption in this alcohol and that in butyl alcohol. The band λ 3455 as about 10 Angström units wide and is quite weak, λ 3485 is of about the same width and is much stronger, λ 3515 is very weak, $\lambda\lambda$ 3545 and 3570 are of about the same intensity and each 10 Angström units wide. There seems to be a very weak band at about λ 4300. Wide and very diffuse bands appear at $\lambda\lambda$ 4550, 5120, 5220, 5250, 5720, 5780, 5800, 5850 and 5890. The four bands last mentioned are of about equal intensity.

The general characteristics of the absorption spectrum of neodymium chloride in isobutyl alcohol are the weakness and diffuseness of the bands in general, their different relative intensities compared with butyl alcohol bands, and their slightly greater wave lengths. The butyl alcohol bands are very much finer and sharper than the isobutyl alcohol bands. In general, it seems that the shorter the wave lengths of the solvent bands the finer and sharper are these bands.

Another spectrogram taken of a solution containing a much longer layer contains the following bands: The β group, λ 4270, a very weak and narrow band; λ 4290, a weak band about 6 Angström units wide; λ 4310, the strongest band in the group, being a little stronger than λ 4290; λ 4330, weak and quite diffuse, completing the bands of this group; a very wide (50 Angström units) diffuse band appears at λ 4450; the γ group consists of bands about 20 Angström units wide at λ 4700, λ 4730, λ 4780, λ 4830 and λ 4880, this band being very weak; the δ bands at λ 5150 and λ 5260 are about 80 Angström units in width, and consist of smaller bands that appear practically fused together, some of the finer bands being at λ 5215, λ 5230, λ 5250 and λ 5300; the ε group is composed of the following bands: λ 5740 rather weak, λ 5810 strong, λ 5850 strong, λ 5890, λ 5920, λ 5950 very weak, λ 5995 very weak, and λ 6020 very weak.

The ultraviolet absorption of isobutyl alcohol is very con-

siderable and prevents the α bands from being shown very plainly. The smaller bands are all more numerous, although weaker than in most other solvent spectra.

Neodymium Chloride in Ether.—Neodymium chloride is only very slightly, if at all, soluble in ordinary ether. By adding a small amount of a concentrated solution of neodymium chloride in methyl alcohol to ether, a solution about 0.01 normal was obtained. At about 10° this solution is transparent and its absorption was photographed. Heated to about 35°, a white precipitate was formed, making the solution quite opaque. When cooled again the solution became transparent. A solution of this kind might serve to give us a better knowledge of the constitution of aggregates. Suppose it could be shown, spectroscopically, that the neodymium chloride aggregates existed in the ether as the methyl alcoholate, and that when the cloud was formed the ether solution was completely freed from any neodymium salt. The number of cloud particles could easily be counted with an ultraviolet microscope, and the size of the neodymium aggregates thus approximately determined. A study of the Brownian movements and the growth of such a cloud would also be interesting. It might be possible in some case to obtain a transparent solution of colored solvates in a solvent having the same index of refraction and density as the solvate, but not miscible with it; and by heating such a solution the liquid of the solution and the solvate might mix at higher temperatures and the resultant salt aggregate, if insoluble, would then be precipitated.

Neodymium Nitrate in Propyl Alcohol.—The absorption bands of this spectrum are quite diffuse and present a sort of washed-out appearance.

The α group consists of three bands, the inner band being the wider and weaker. These bands are nearly 20 Angström units wide and are located at λ 3455, λ 3500 and λ 3585. The β group consists of but a single band about 12 Angström units in width at about λ 4268. The γ and other bands in that region are very broad and weak. The δ group is resolvable into the single bands λ 5100 and λ 5220. For the greater concentrations, however, two bands can be distinguished near

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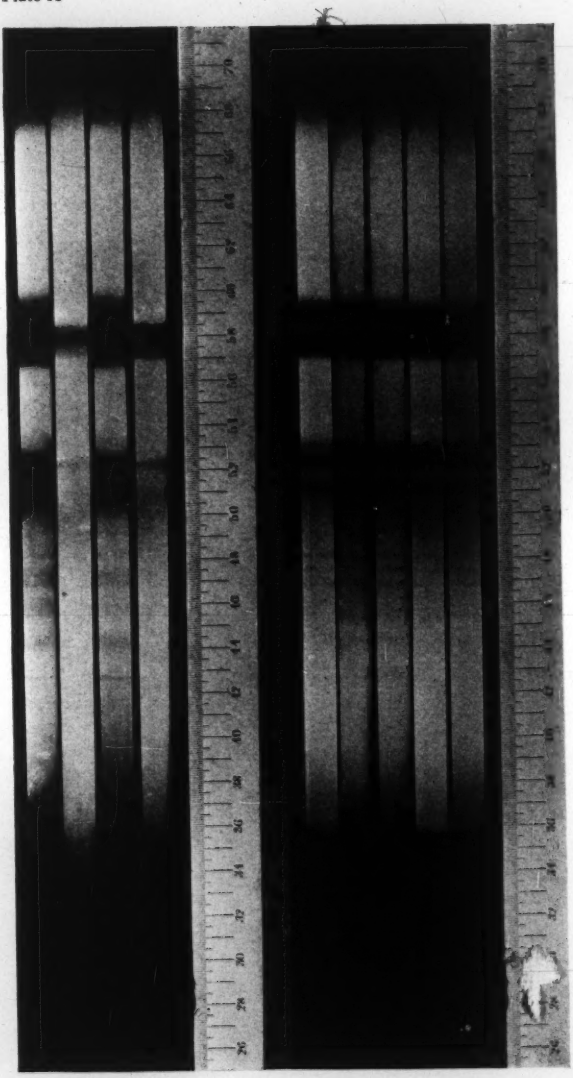
Plate II



A B

the center of λ 5220, being at about λ 5220 and λ 5235. The ε group consists of the hazy bands λ 5700, λ 5750, λ 5780 and λ 5810.

Neodymium Nitrate in Isopropyl Alcohol.—The absorption spectrum resembles quite closely in the general diffuseness the propyl alcohol spectrum previously described.

The α group consists of three hazy bands at λ 3460, λ 3505 and λ 3535. Each of these bands is about 15 Angström units in width. The β band is weak, being located at λ 4270. Bands appear at λ 4430, λ 4690 and λ 4730. The δ group consists of a band at λ 5100 and one at λ 5230. The latter consists of a wide, diffuse, short wave-length component, and two finer bands that resemble very closely the corresponding propyl alcohol bands. The ε group consists of a weak hazy band at λ 4720, and two stronger bands at λ 5790 and λ 5810.

Neodymium Nitrate in Butyl Alcohol.—The absorption spectrum of neodymium nitrate in butyl alcohol is given in the first two strips of *A*, Plate II. The general characteristic of the bands is their general diffuseness.

The α group consists of three diffuse bands, the outer bands being much the strongest at $\lambda\lambda$ 3450, 3500 and 3540. The β group consists of a band at about λ 4265, and a very weak band at about λ 4280. Weak and diffuse bands appear at λ 4420, λ 4690, λ 4730 and λ 4820. The other bands are at λ 5090, λ 5220, λ 5710, λ 5800 and λ 5930.

The absorption spectrum of neodymium nitrate in butyl alcohol resembles very closely the spectrum in isopropyl alcohol, but is quite different from the spectrum in isobutyl alcohol.

Neodymium Nitrate in Isobutyl Alcohol.—The absorption spectrum of neodymium nitrate in isobutyl alcohol is similar to that of the chloride in the same alcohol. The bands in some cases are not so wide, but they are all quite weak when they first appear in the spectrum. The ultraviolet absorption was so great that in the photograph taken the α group does not appear at all. At λ 4285 appears a weak double band about 15 Angström units wide. These bands are so close to one another that it is difficult to be certain that they are separate

bands. There are also very weak bands at λ 4305 and λ 4325. The β group of the chloride in isobutyl alcohol is very different in its structure from that of the β group of the nitrate. A very weak band appears at λ 4450 and λ 4600, which is about 80 Angström units wide. The γ group consists of weak bands, each about 20 Angström units in width, at $\lambda\lambda$ 4715, 4750, 4770 and 4850. The δ group consists of the wide and very hazy band at λ 5120, two comparatively weak bands at λ 5215 and λ 5230, and three strong bands that practically merge into each other at λ 5245, λ 5255 and λ 5275. The ε group forms a single wide band extending from λ 5730 to λ 5900. Very hazy and weak bands appear at λ 6000, λ 6050 and about λ 6800.

The composition of the various groups of the nitrate isobutyl bands is quite different from the chloride bands. This is a general phenomenon, the nitrate bands being quite different from the chloride and bromide bands in the same solvent.

Neodymium Nitrate in Acetone.—The absorption spectrum of neodymium nitrate in acetone also consists of wide, diffuse and weak bands. The ultraviolet absorption is large.

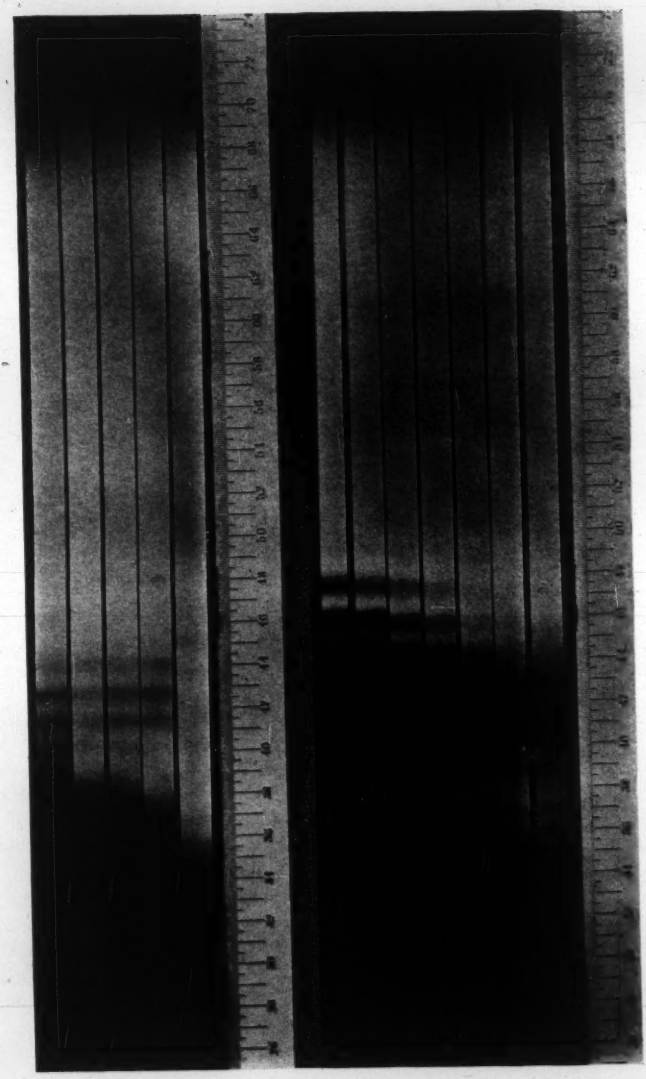
The following bands appear: λ 4285 very weak, λ 5130, λ 5250, λ 5750 and λ 5840.

Neodymium Nitrate in Ethyl Acetate.—The absorption bands of this spectrum are in general quite diffuse. The α group consists of three hazy bands, the middle one being much the weakest, at $\lambda\lambda$ 3455, 3500 and 3540. The β group consists of a single band about 15 or 20 Angström units wide at about λ 4270. The bands at $\lambda\lambda$ 4440 and 4600 are very broad and weak. The γ group is quite different from the γ group of other solvents in that the bands are not even approximately of the same intensity or at equal distances from each other, being at about λ 4710, λ 4730 and λ 4830. The δ group consists of λ 5120, λ 5210, λ 5240 and λ 5260. The ε group consists of $\lambda\lambda$ 5700, 5750, 5780 and 5810. These bands are very diffuse, about 20 Angström units wide, and the latter two are much the stronger. A band also appears at λ 5980.

The absorption spectrum of neodymium nitrate in methyl acetate is identical with that in the ethyl ester.

Neodymium Acetate in Acetone.—The absorption spectrum

Plate III



of neodymium chloride in acetone has bands that are much more diffuse than the corresponding water bands. Similarly, the acetone bands of the acetate are more diffuse than the water bands, and both spectra are more diffuse than the chloride spectra.

The α group of the acetate in acetone apparently consists of but a single band, quite weak, at λ 4270 and about 15 Ångström units wide. The region λ 4300 to λ 5100 is practically continuous, the bands appearing there being so weak and diffuse that they can hardly be detected. The δ group consists of a wide diffuse band at λ 5110 and finer bands at λ 5200 (weak), λ 5235, λ 5250 and λ 5260, the latter three practically blending into one. The ε group extends from λ 5720 to λ 5860, this absorption showing a weak band at λ 5730, about 30 Ångström units in width. From the above description it will be noticed that there is a strong ultraviolet absorption (reaching to λ 3900), and that the neodymium bands themselves are very wide and diffuse.

Neodymium Acetate in Formamide.—The absorption bands of this solution are quite wide and diffuse, but not as much so as the bands of the acetate in acetone. The ultraviolet absorption is so strong as to prevent the appearance of the α group. The β group consists of a band at λ 4285 which is about 10 Ångström units wide. The bands $\lambda\lambda$ 4440, 4690, 4750, 5110 and 5230 are wide, diffuse and, with the exception of the latter, very weak. The ε group consists of four diffuse bands that run into each other at $\lambda\lambda$ 5710, 5740, 5790 and 5830.

The Absorption Spectrum of Solutions of Certain Salts of Uranium.—For a full discussion of the absorption spectra of a large number of uranium solutions the reader should consult Publication No. 130 of the Carnegie Institution of Washington. In the following pages only a few solutions are discussed, these being for the most part solutions of the uranyl salts in some of the organic solvents. This was taken up because corresponding neodymium solutions were being investigated, and it was thought to be of some interest to study a few uranyl solutions in the same way. In the description of the bands of uranium solutions it must be remembered that the terms

wide, fine, sharp, narrow, broad, etc., are relative to other uranyl or uranous bands and not to neodymium or samarium bands. A sharp uranyl band would be a very wide and hazy neodymium band.

Uranyl Chloride in Propyl Alcohol.—The absorption bands of the propyl alcohol solution are quite strong and appear at the following positions: λλ 3980, 4100, 4230, about 4400 (this band is apparently double), 4580, 4750 and 4910. The upper strip shows quite well the difference in intensity of the *a* and *b* bands. In this strip the *b* band is very broad and strong, running from λ 4690 to about λ 4820. On the other hand, the *a* band is quite weak and is not more than about 40 Angström units in width.

Uranyl Chloride in Isopropyl Alcohol.—The blue-violet band is seen to be quite prominent, its middle coming at about λ 4350, about 100 Angström units farther towards the red than for the aqueous solutions. The uranyl bands are very weak and diffuse, being much more so than for the propyl alcohol solution. The *a* band does not appear on the spectrogram. The following bands show: λ 4100, λ 4250, λ 4360 (these two bands practically merge into one another), λ 4560 and λ 4750.

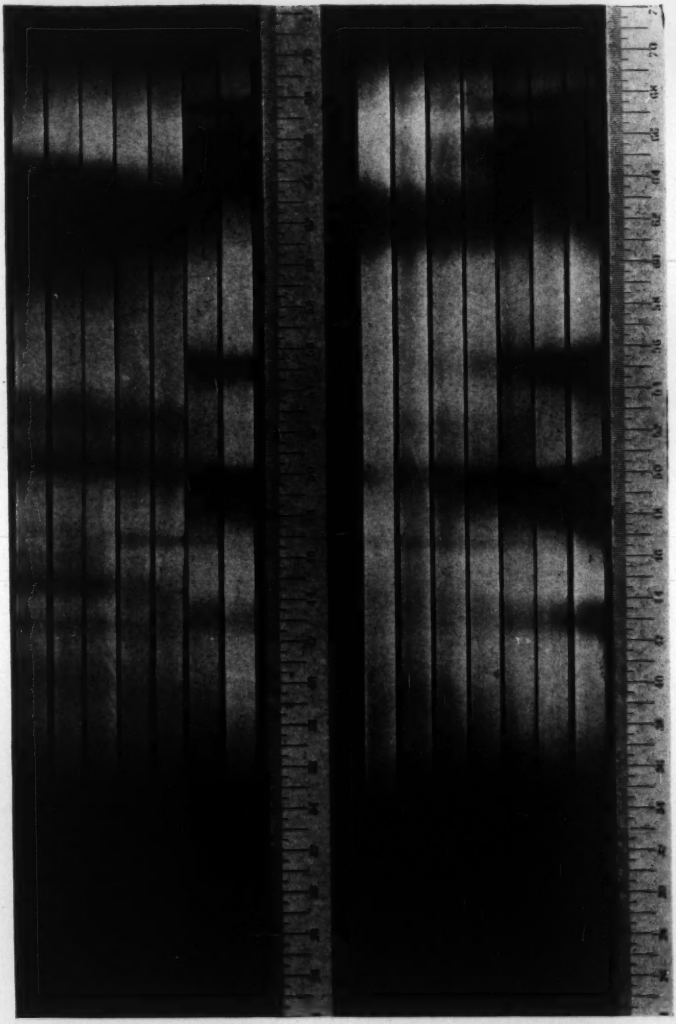
Uranyl Chloride in Butyl Alcohol.—The following bands can be distinguished from the general absorption: λλ 3850, 3960, 4100, 4240, 4390, 4560, 4750, 4970. The bands are all very diffuse, the last band being about 150 Angström units in width.

Uranyl Chloride in Isobutyl Alcohol.—The spectrogram shows the following uranyl bands: λλ 4400, 4560, 4720 and 4900.

Uranyl Chloride in Ether.—The following uranyl bands have been photographed for a solution of uranyl chloride in ether: λλ 4040, 4160, 4300, 4444 and 4630. The solubility of uranyl chloride in dry ether is very small.

Uranyl Chloride in Methyl Acetate.—The uranyl bands show quite strongly in the methyl acetate solution of the chloride. The bands are as follows: λ 4030(*g*), λ 4160(*f*), λ 4280(*e*), λ 4440(*d*) (this band may be double and thus really represent *de* instead of simply *d* as given above), λ 4620(*c*), λ 4790(*b*) and λ 4920(*a*). The *a* band is very weak, compared with the

Plate IV



A B

b band. Beyond the *a* band towards the red, there is a very weak band which is so weak that it is very difficult to distinguish it from the absorption of the blue-violet band itself.

Uranyl Chloride in Ethyl Acetate.—The absorption bands are very strong and are quite sharp. The wave lengths and general appearance of the bands are practically the same as that of the methyl ester solution previously described.

Uranyl Chloride in Formamide.—The uranyl bands appear quite strong, especially the long wave-length bands. The three bands in the second strip appear of about equal intensity at λ 4450, λ 4650 and λ 4840. The latter band is probably the *b* band. The *a* band does not appear at all on the spectrogram.

Uranyl Nitrate in Propyl Alcohol.—The absorption bands are quite strong and sharp and appear as follows: $\lambda\lambda$ 3640, 3750, 3850, 3970, 4080, 4190, 4320, 4470, 4640 and 4820. The latter band is probably the *a* band, as it is very much narrower than the band at λ 4640.

Uranyl Nitrate in Acetone.—The photograph of the absorption spectrum of uranyl nitrate in acetone showed only three bands. These bands are quite narrow, but were not as sharp as the chloride bands. They are at λ 4510, λ 4660 and λ 4830.

Uranyl Nitrate in Methyl Acetate.—The bands are rather weak, appearing at $\lambda\lambda$ 3900, 4000, 4110, 4220, 4340 and 4480.

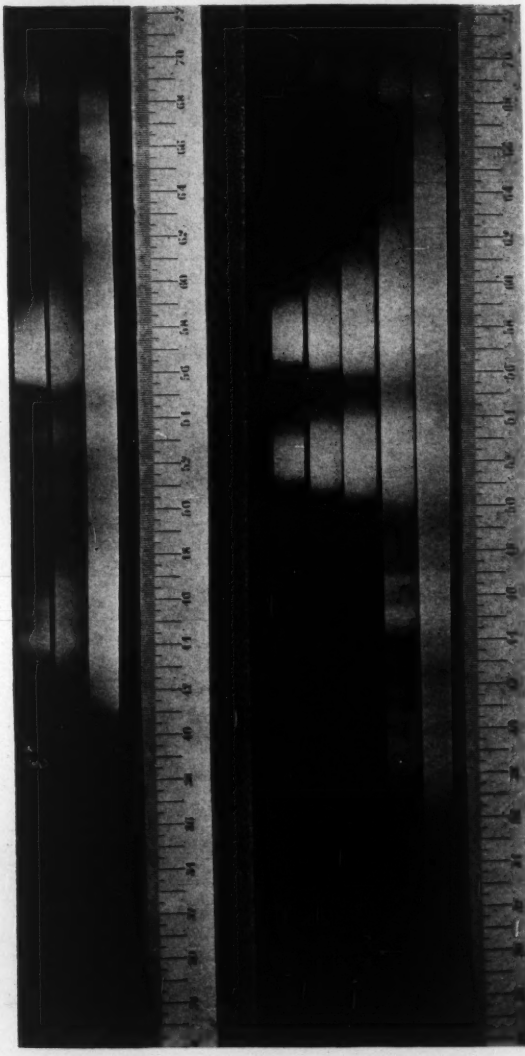
Uranous Chloride in Propyl Alcohol.—The absorption bands are all quite strong, especially the uranyl bands. The uranyl bands shown most prominently are those at λ 4590 and λ 4750, each about 80 Angström units wide, and a very wide band at λ 4950, about 150 Angström units wide. Two fine bands appear at about λ 5190 and λ 5210. These bands are about 10 Angström units in width. A band at λ 5500 is about 120 Angström units in width. A group of three narrow bands appears at about λ 5720, λ 5750 and λ 5770. The middle band is the strongest one of the group, and is about 15 Angström units wide. Absorption maxima appear at about λ 6100, λ 6270 and λ 6520. This whole region is one of more or less general absorption, due to the above very wide bands. The band at λ 6720 is very similar to the uranyl bands at λ 4590

and λ 4750. The general appearance of these uranous bands in the red is very much like that of the aqueous uranous bands.

Uranous Chloride in Isobutyl Alcohol.—The uranous bands of this absorption spectrum appear quite sharp, especially when they are broad, as is the case in the upper strips of this spectrogram. The first strip shows a double band at about λ 4300. These bands practically merge, especially in the other strips, the shorter wave-length band being much more intense. Quite a sharp band appears at λ 4950, with a broad region of absorption on the violet side. With a larger amount of salt this absorption is greatly increased, resulting in a very great widening of the band on the violet side, while the red side widens but little. A band appears at λ 5480, a weak band at λ 6300, a strong band from λ 6400 to λ 6600, and a strong band at λ 6720. The spectrogram shows the total absence of the uranyl bands, and very slight absorption in the region of the ultraviolet. The upper strip shows the wide uranous bands very sharply indeed.

Uranous Chloride in Methyl Acetate.—From the absorption spectrum it is apparent that the uranyl salt has been largely reduced, since the uranyl bands do not show at all. Uranous bands appear at λ 4300 (about 120 Angström units in width). There is a region of strong absorption extending from about λ 4700 to λ 5100, with the strongest absorption in the longer wave-length portion of this region, resulting in a much greater widening of the band towards the violet as the amount of salt in the beam of light is increased. There is a band at λ 5500 about 150 Angström units wide and the red bands appear. The red bands are both rather wide, the stronger and narrower one being at λ 6730. In one strip the absorption runs from λ 6400 to about λ 6760. As the absorption increases this red absorption region widens very unsymmetrically towards the region of shorter wave lengths. This solution, like most other clear uranous solutions, shows very little general absorption in certain regions of the spectrum. Even the general absorption in the ultraviolet is not so very great. When a large amount of the solution is placed in the beam of light, considerable light still

Plate V



A B

passes through, and the edges of the absorption bands appear quite sharp.

The Absorption Centers of Uranium Spectra

Important results will probably be obtained by a study of uranyl and uranous compounds at low temperatures. It might be possible to obtain aggregates of sufficient size to be seen by the ultraviolet microscope, or to be observed in a manner somewhat similar to that of the scintillation method of observing the α rays on a phosphorescent screen. The uranyl aggregates could be illuminated by flashes of ultraviolet light, and by proper sector arrangements the aggregates could be viewed in the intervals between the illumination. These aggregates should then appear as centers of the green uranyl phosphorescence. Neodymium compounds in phosphorogens could possibly be treated in the same manner. These salts should also be studied when under bombardment by β rays, if they do not show any effect by α rays. Recent studies of phosphorescent screens subjected to α-ray bombardment have led to the belief that these substances are composed of aggregates.

The Absorption Spectrum of Gadolinium

Very little has been done on the absorption spectrum of gadolinium. A dilute nitrate solution in a 10 mm. layer showed several weak bands at λ 3500 to λ 3390, with a maximum at λ 3470. A weak band appeared at λ 3300 to λ 2890, and continuous absorption commenced at about λ 2200. According to Soret there is a band from λ 2800 to λ 2450.

Gadolinium Chloride in Water.—The absorption spectrum of a solution of gadolinium chloride, 1.407 normal, was photographed; the depths of cell, starting from the lowest strip, were 2, 10, 15, 22, 22 and 100 mm. The spectrogram shows that there is quite a strong, general absorption in the ultraviolet, amounting to several hundred Angström units in the case of the 2 mm. length of layer, transmission beginning at about λ 2700. For the 100 mm. length of layer this absorption extends to about λ 3700, the edge of the transmission being very broad.

The photograph shows, besides this general absorption, two very sharp bands at λ 2925 and λ 2980. These appear clearly for the 10 mm. layer. For the 100 mm. layer a weak band, about 25 Angström units in width, appears at λ 3910. A very weak band appears at λ 3970. This band is so weak that it can hardly be seen in the original film.

Gadolinium Chloride in Ethyl Alcohol.—The absorption of an 0.8 normal solution of gadolinium chloride in ethyl alcohol was studied; the depths of cell were 2, 4, 9, 18, 27 and 27 mm.

One of the most pronounced characteristics of the absorption of this alcoholic solution is the enormous absorption in the ultraviolet, compared with the aqueous solution. The edge of this absorption is very diffuse. It extends to about λ 3000 for the 2 mm. solution, and to about λ 4400 for the 27 mm. solution.

The only characteristic part of the absorption spectrum is a very diffuse band at λ 4360. The band is gradually included in the region of general absorption as the depth of cell is increased.

It will be noticed that the absorption spectra of the alcohol and aqueous solutions are very different indeed.

The Absorption Spectrum of Dysprosium

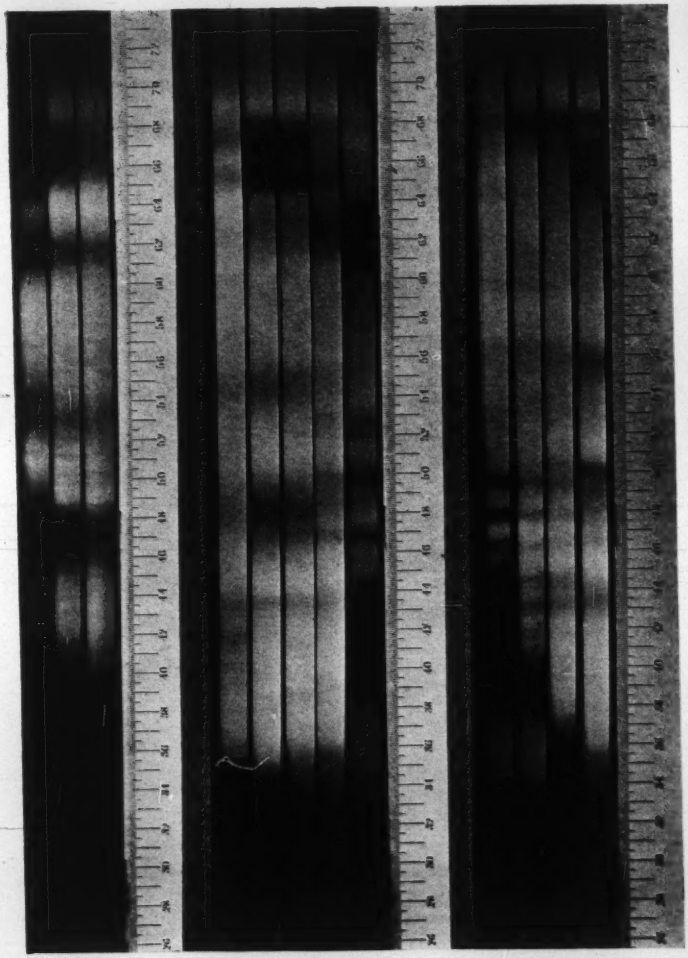
Very little work has been published on the absorption spectrum of dysprosium. Lecoq de Boisbaudran[1] has described the following bands arranged according to the intensity of the bands: $Dy\alpha$, $\lambda = 4515$; $Dy\beta$, $\lambda = 4750$; $Dy\gamma$, $\lambda = 7565$; $Dy\delta$, $\lambda = 4275$.

Urbain[2] has observed only λ 4740 and a weak band at λ 4530 to λ 4500.

Dysprosium Chloride in Water.—The absorption in the ultraviolet is very small for aqueous solutions of dysprosium chloride, even when the depth of cell is as great as 21 mm., and the concentration is 1.86 normal. The general appearance of the bands is much the same, although they vary greatly in intensity. The edges are quite sharp, although none of the

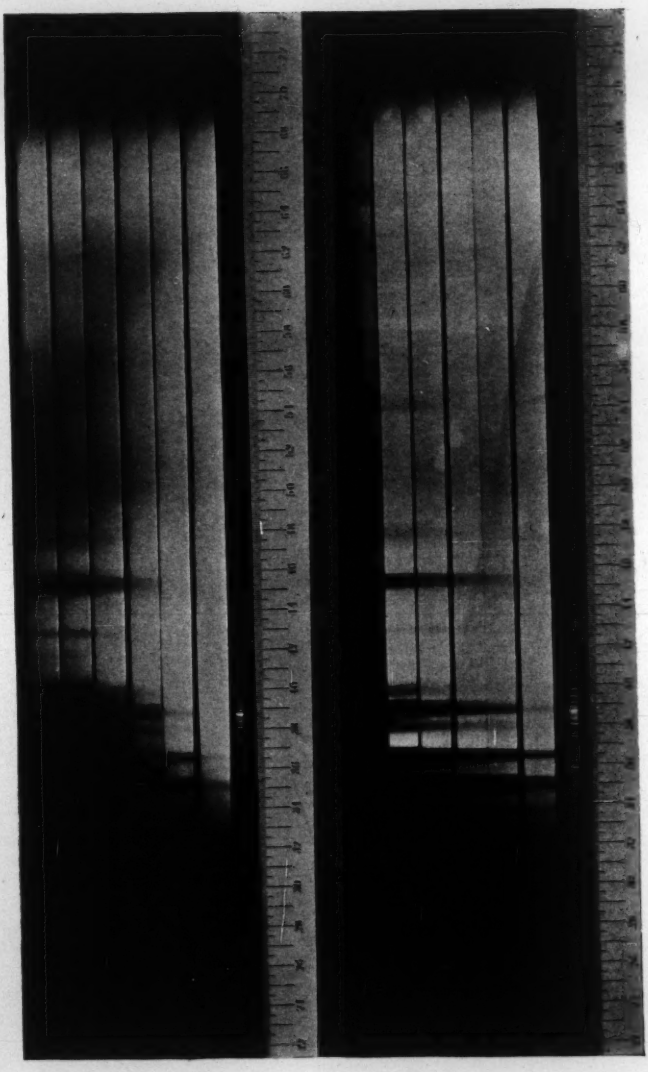
[1] Compt. rend., **102**, 1005 (1886).
[2] Ann. chim. phys., **19**, 244 (1900).

Plate VI



A B C

Plate VII



A B

bands are as sharp and clear as the neodymium water band, λ 4271.

The first band observed in the ultraviolet is λ 3130. As can be seen from the spectrograms the bands in the ultraviolet are by far the strongest in the spectrum. The band λ 3130 is one of the strongest of these ultraviolet bands, and is about 40 Angström units wide. The next band at λ 3260 is about 20 Angström units wide, and is quite weak. It is very similar and of the same order of intensity as the bands at $\lambda\lambda$ 3470, 3670, 3690, 3800, 3850, 4170, 4340, 4400 and 4430. Of these bands, the latter two are the strongest. The band λ 3390 is the strongest band in the whole spectrum. It possesses sharp edges and is over 50 Angström units in width, while the strong band λ 3535 has only a width of 30 Angström units. The band λ 3760 is also quite strong and has a width of about 25 Angström units. Other bands appear faintly at $\lambda\lambda$ 4650, 5300 and 6350, but these are so weak that their positions can hardly be measured. The band at λ 3970 is very broad and weak, and shows best in the fifth strip of the photograph.

In the last strip of 100 mm. depth, quite a number of new bands appear. The ultraviolet absorption has become so strong that the whole region to λ 4050 is absorbed. The band at λ 4160 is apparently double, being much more intense on the violet side. The bands at λ 4190 and λ 4220 are much weaker, the former almost merging into λ 4160. Absorption bands extend from λ 4250 to λ 4300, λ 4450 to λ 4580, λ 4680 to λ 4820. Very weak bands appear at $\lambda\lambda$ 4840, 4890, 4930, 4960, 5425, 5460, 5490, 5520, 6460, 6570 and 6600. The band λ 5380 is quite strong and almost merges into the other bands in this region. The band λ 6440 is also quite strong. The bands λ 6440 and λ 6460 are very diffuse and almost form a single band.

Dysprosium Chloride in Methyl Alcohol.—The absorption spectrum of a solution of dysprosium chloride in methyl alcohol is given in *A*, Plate VII. The absorption is greater for the alcohol solution, especially the general ultraviolet absorption. Otherwise the relative intensity, number, wave length

and general appearance of the absorption bands are exactly the same as the bands of the aqueous solution.

Dysprosium Chloride in Ethyl Alcohol.—With the exception of the very much greater ultraviolet absorption, the spectra of dysprosium chloride in water, methyl alcohol and ethyl alcohol (*B*, Plate VIII) are very much the same, the ethyl alcohol band at λ 5400 being wider and of greater wave length than the water and methyl alcohol bands at λ 5380.

The fact that this one band should appear of a different wave length in ethyl alcohol, as compared with water, while the other dysprosium bands appear to be the same for both solvents, might be taken to indicate that this band was not due to dysprosium. A difference of this kind might lead to a possible method of ascertaining the presence of the salts of two different elements in solution. In the case of neodymium salts it was found, in general, that if one solvent had one characteristic band, all the solvent bands were more or less characteristic. On the other hand, it must be remembered that in the case of the uranyl bands, the differences for different solvents were usually much greater for the longer wave-length bands. So, in the above case of dysprosium chloride in ethyl alcohol, we may assume that the band λ 5380 may not be due to dysprosium. It may be that the difference in the action of acids on the bands of the spectra of a given salt, or the difference in the spectra as obtained with the same salt in different solvents, will be useful in separating the different elements.

Dysprosium Acetate in Water.—The absorption spectrum of dysprosium acetate (0.4 normal) in water is given in *A*, Plate VIII). The depths of cell were 4, 16, 25 and 34 mm. The spectrum is very similar to that of the aqueous solution of the chloride. The bands are, however, somewhat more diffuse. The wave lengths of the bands, which are comparatively weak, appear to be the same for the chloride and the acetate. The acetate bands widen more to the red, so that when the bands are quite wide the acetate bands appear to be relatively shifted towards the red. The addition of concentrated nitric

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Plate VIII

A B

Plate IX

A B

acid produces little effect on the wave length or the appearance of the dysprosium acetate bands in water.

The Absorption Spectrum of Samarium

The absorption spectrum of samarium has been studied much more extensively than that of gadolinium and dysprosium.

In general appearance the absorption spectra of samarium salts are very similar to those of the dysprosium salts, the strong bands of the spectrum being located in approximately the same violet and ultraviolet part of the spectrum. The general appearance of the individual bands is very similar to that of the dysprosium bands, the samarium bands being, however, somewhat narrower and having sharper edges.

Samarium Chloride in Water.—The absorption spectrum of samarium chloride in water is shown in *A*, Plate IX. The concentration is 1.31 normal and the depths of cell, starting from the lowest strip, are 2, 6, 12, 16, 20 and 100 mm.

From the spectrogram it is seen that for the aqueous solution the ultraviolet absorption is very small indeed. A weak and apparently quite wide band appears at about λ 3050. For the 6 mm. depth of cell, second strip, bands appear at $\lambda\lambda$ 3200, 3320, 3510, 3630, 3910, etc. The other bands are quite weak. Of the above bands, λ 3910 is by far the strongest of all the samarium bands. For the 20 mm. layer the following appear: λ 3420 (diffuse), about 20 Angström units wide), λ 3470 to λ 3540, λ 3550 very weak, λ 3570 very weak, λ 3600 to λ 3660, λ 3720 very weak and wide, λ 3770 weak, λ 3800 (about 20 Angström units wide), λ 3860 to λ 3945, λ 3970, λ 4050, λ 4070, λ 4320 very wide and weak, λ 4540 (about 40 Angström units wide), λ 4640 to λ 4750 is a region consisting of two diffuse bands that practically run together, λ 4800 weak, λ 5110 weak. Other bands appear in the region of longer wave lengths, but they are very weak.

A 100 mm. strip showed complete absorption of wave lengths shorter than λ 4130. Bands appeared from λ 4210 to λ 4370; a band about 30 Angström units wide at λ 4420; a band from λ 4470 to λ 4840; λ 4890 to λ 4950; λ 4200, λ 4230 (these two

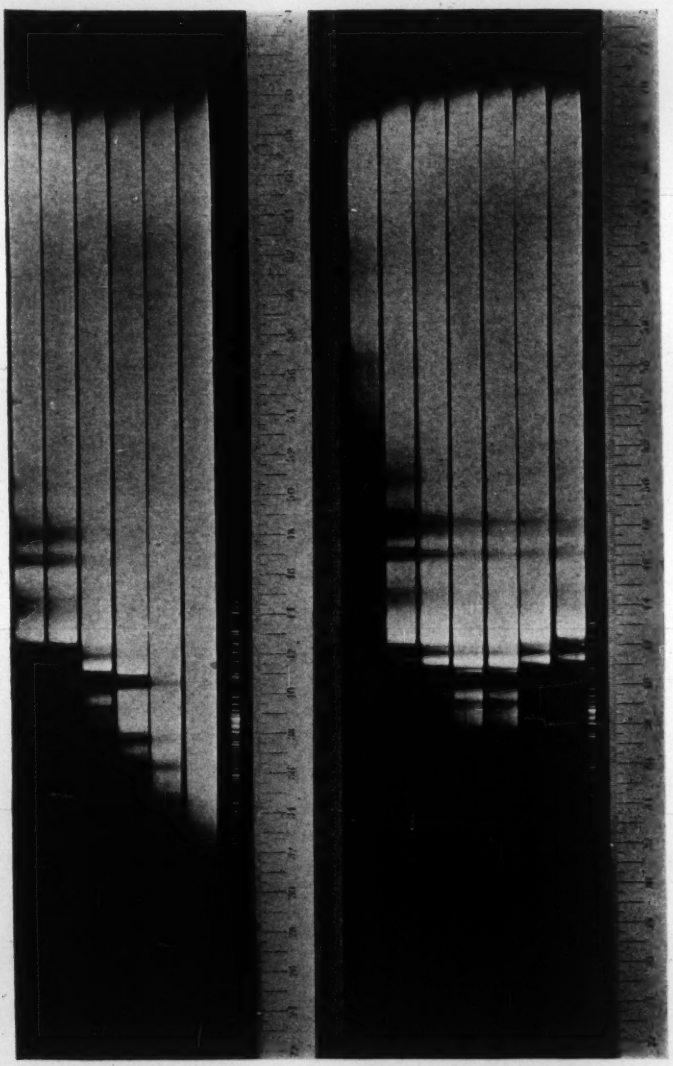
bands are of about the same intensity, rather diffuse and about 20 Angström units wide); λ 5500, λ 5525; these bands are very similar to the preceding pair, being, however, considerably more intense.

Samarium Nitrate in Water.—The absorption bands of samarium nitrate in water have almost the same characteristics, relative intensity, wave lengths, etc., as the water bands of samarium chloride.

Samarium Chloride in Methyl and Ethyl Alcohols.—The absorption spectrum of samarium chloride in methyl alcohol, *B*, Plate IX, is so similar to that of this salt in ethyl alcohol, *A*, Plate X, that only the former will be described in detail. It will be seen from the spectrograms that the general absorption in the ultraviolet and violet, in the case of the ethyl alcohol solution, is very much greater than in the case of the methyl alcohol solution.

B, Plate IX, represents the absorption of a normal solution of samarium chloride in methyl alcohol, the depths of cell being 2, 5, 9, 18, 27 and 27 mm. The last spark spectrum was taken with the solution removed, simply for the purpose of making wave-length measurements. The first strip shows the following bands: λ 3200, λ 3330, λ 3500, λ 3540, λ 3640, λ 3910, λ 3925, and some weaker bands farther towards the red. The third strip shows the following bands: λ 3200, quite weak; λ 3330, λ 3350, λ 3430, and λ 3450, very weak and diffuse, appearing almost as a single band; λ 3500, λ 3540, λ 3570, λ 3640; λ 3910, the strongest band in the spectrum, about 35 Angström units wide; λ 3950, about 10 Angström units wide; λ 3970, about 6 Angström units wide; λ 4060 and λ 4100, each about 30 Angström units wide and quite weak. Other bands are easy to see and are described for the last strip. In this strip the ultraviolet absorption is complete to λ 3350. In addition to the bands mentioned above there were bands at $\lambda\lambda$ 4290 weak, 4310 weak, 4350 weak, 4410 weak; 4520, 4545, 4570; this triple group is perfectly symmetrical, the middle band being much the strongest; 4650, 4705 and 4760, each about 40 Angström units wide, diffuse and weak with the middle band having the greatest intensity; 4810,

Plate X



A B

about 10 Angström units in width; 4920, quite weak and diffuse; and 5200 very weak. No other bands in the longer wavelength region are visible in addition to those described.

Samarium Chloride in Water and Ethyl Alcohol.—The absorption spectrum of samarium chloride in mixtures of water and ethyl alcohol is given in *B*, Plate X. The change from the alcohol to the water spectrum can easily be seen in the shift of the bands of Strip 1 compared with Strip 2 in *B*, Plate X. The very great persistency of the water bands is shown, since in this case (Strip 2) only about 5 per cent. of water is present. The band λ 3970 seems to be a characteristic water band. It seems, therefore, that the samarium bands behave in the same way as the neodymium bands, although there is no single band that shows the effect as clearly as the neodymium λ 4271 water band, and the corresponding λ 4290 alcohol band. Since the water bands are so persistent it would be very interesting to carry this work to temperatures almost as low as the freezing point of alcohol. In general, a lowering of temperature has increased the persistency of the water bands.

SPECTROPHOTOGRAPHY OF CHEMICAL REACTIONS

Prior to these investigations[1] very little work had been done on the effects produced on the absorption spectrum of a salt in solution when acids and various other reagents that bring about chemical reactions were added. Indeed, much of our knowledge of what is in solution is obtained indirectly rather than by a direct knowledge of the composition of compounds while in solution. Considerable work on the effect of the introduction of certain radicals, groups, etc., on the absorption spectra of organic compounds has been done.

It is true that a few observers had noticed that in some cases different salts had bands of different wave lengths, when dissolved in the same solvent. A typical example of this kind is given in the following table. Then again, observers had noted that the bands of one salt of a metal were finer and sharper than the bands of another salt (for example, neodymium chloride as compared with the nitrate in water), but, as far as we know, no effort has been made to study what changes

[1] Publication 130, Carnegie Institution of Washington.

in the bands resulted as one salt of a metal was changed into another salt.

The following table gives the absorption bands of some double acetates of uranyl, according to Morton and Bolton:[1]

NH_4	4620	4455	4310	4200	4075
Ba	4625	4465	4330	4200	4075
Co	4625	4465	4335	4200	4080
K	4625	4460	4320	4200	4070
Li	4620	4455	4320	4205	4080
Mg	4627	4480	4337	4215	4085
Na	4620	4453	4310	4185	4055
Rb	4625	4465	4315	4202	4080
Sr	4627	4480	4335	4205	4075
Tl	4640	4480	4320	4205	4085
Zn	4655	4490	4340	4325	4100

One of the purposes of the present research is to study one group of bands throughout a long series of reactions. The first group of bands to be studied in this way was the uranyl bands. Although not completely followed, and not identified with certainty in every case, yet for aqueous solutions, at least, it has been possible to designate these bands as *a*, *b*, *c*, *d* .... and to follow each band as the salt is changed from acetate to nitrate, from nitrate to chloride, from chloride to sulphate, etc. It is found in all these changes that the individual uranyl bands undergo a *gradual shifting of their position in the spectrum*. Various chemical changes have been accompanied by characteristic changes in the absorption spectrum, e. g., a narrowing of the bands, a shifting of the bands to the violet, etc. It is natural to try to correlate as many of these characteristics as possible, but as yet not enough work has been done to furnish many generalizations. It may be said, qualitatively, that in many instances a shifting of the bands towards the violet is often accompanied by a narrowing and sharpening of the edges of the bands. This is a general characteristic also of the temperature effect, since a lowering of the temperature of an absorbing compound is nearly always accompanied by a narrowing of the absorption bands and a slight shifting towards the violet.

[1] Chem. News, **28**, 47, 113, 164, 233, 244, 257, 268 (1873).

Again, it is natural to inquire whether the same chemical reaction produces the same changes in the absorption spectra when this reaction takes place in different solvents. Unfortunately there are not many examples of this kind that can be tested. In general, the absorption bands of different salts in the same solvent are practically the same, so that a chemical reaction cannot be photographed spectroscopically. It was for this reason that a considerable number of absorption spectra has been mapped. Unfortunately, a number of solvents showing a difference in the absorption spectra of different salts is not very well suited for this kind of work. Some very good examples, however, have been found, and these will soon be studied. Acetone was found to give a greater difference between the absorption spectra of uranyl nitrate and the other uranyl salts than water; and as the uranyl acetone bands are very sharp and these solutions can be studied at very low temperatures, this solvent offers exceptional advantages for making a comparison between the same chemical reaction in the two solvents.

The closely related problem as to whether apparently similar chemical reactions for different salts in the same solvent are really similar has already been answered in some cases in the negative. We have seen that the chemical reaction that takes place when uranyl chloride has been changed to uranyl nitrate has resulted in a narrowing and sharpening of the uranyl bands, and a gradual shifting of these bands towards the violet. The same change of neodymium chloride to neodymium nitrate in water results in the bands being made broader and more diffuse, and in some cases these bands are slightly shifted towards the red.

It must be stated that the study of the changes that take place in the neodymium bands has been too complicated for the present research. No other element shows such an extremely wide diversity in the structure of its various groups of bands, and at present no examples have been found where any bands can be traced throughout chemical reactions. The changes seem rather to be connected with a change in the relative intensity of bands in the same group, and, therefore, a

shifting of the center of gravity of the absorption of the group itself. This may be true also of the uranyl bands, since it is known that the uranyl bands break up into much finer bands at low temperatures. At any rate, the changes in the uranyl bands at ordinary temperatures, when chemical reactions take place, is comparatively simple compared with the same changes in the case of the neodymium bands.

It is very important that a careful study be made of a series of chemical transformations of neodymium salts (especially at low temperatures). For instance, it has been shown that different anhydrous neodymium salts possess very different absorption spectra. Comparison between the spectrophotographs of dry chemical reactions should be made and compared with the same reactions in various solvents. As soon as we know what physical and chemical conditions are connected with given spectroscopic changes, then a study of the absorption spectra of crystals should be of aid in giving us an insight into the physical and chemical conditions within crystals.

The following cases of chemical reactions are treated from the standpoint of the theory of aggregates, as fully developed in the general remarks at the end of this paper. It may be possible to obtain some knowledge of these aggregates by other methods. In the study of α, β and γ rays it is found that, in general, the absorption of these radiations depends on the atomic structure of the matter they traverse, rather than on the molecular structure. There may possibly be some exceptions to this rule. For instance, uranium and thorium salts emit α rays, these rays probably coming from the uranium and thorium atoms themselves, before they break down into the next radioactive product. If we had a very thin layer of uranium or thorium salt, it would be expected that the range of most of the α particles would be less if the uranium or thorium existed as an aggregate or in the simple molecular condition. It might, therefore, be found that the range of the α particles from uranyl nitrate would be related to the wave length of the uranyl or uranous absorption bands. Knowing something of the electromagnetic forces necessary to alter the path of the α particles, it might be possible to find some of

the properties of the fields of force that exist in the neighborhood of the uranium and thorium atoms, and the correlated effects upon the frequency of the absorption bands. Similar effects might be obtained in the case of the β and γ rays. The particles of the active deposits might also be used as nuclei about which aggregates would be formed.

Another possible method of studying aggregates is by the phosphorescence produced by α and β rays. The effect of changes in temperature could also be taken up in this connection. Several workers have concluded that the phosphorescence produced by the bombardment of certain kinds of screens by α rays is not due to the breaking up of crystals along lines of planes of cleavage, but that it is due to the breaking up of aggregates that are of approximately molecular dimensions, and that unless such aggregates are present, no phosphorescence is produced. For example, pure zinc sulphide is not phosphorescent, but when there are impurities present phosphorescent scintillations can be produced. It is probable that in most phosphorescent screens there are a large number of active centers present. When the centers on the surface are destroyed, those farther in the screen will become sources of scintillations. When the screen is new, each bombarding α particle probably excites a considerable number of centers. As the bombardment is continued the number of centers excited by each α particle decreases, although each particle will excite one or more centers, so that only the intensity and not the number of scintillations is decreased. The calculated diameters of the active centers of zinc sulphide and willemite are of molecular magnitude, whereas, in the case of barium platinocyanide, the diameter is about a hundred times this size. Marsden[1] has found that the number of scintillations is slightly less at 100° than at 15°.

It would be interesting to prepare salts so that various solvates and aggregates would be formed, and then study the scintillations produced by them. The above suggestions are made, since they are along somewhat different lines than those usually followed in the study of solutions.

[1] P. Roy. Soc., [A], **84**, 548 (1910).

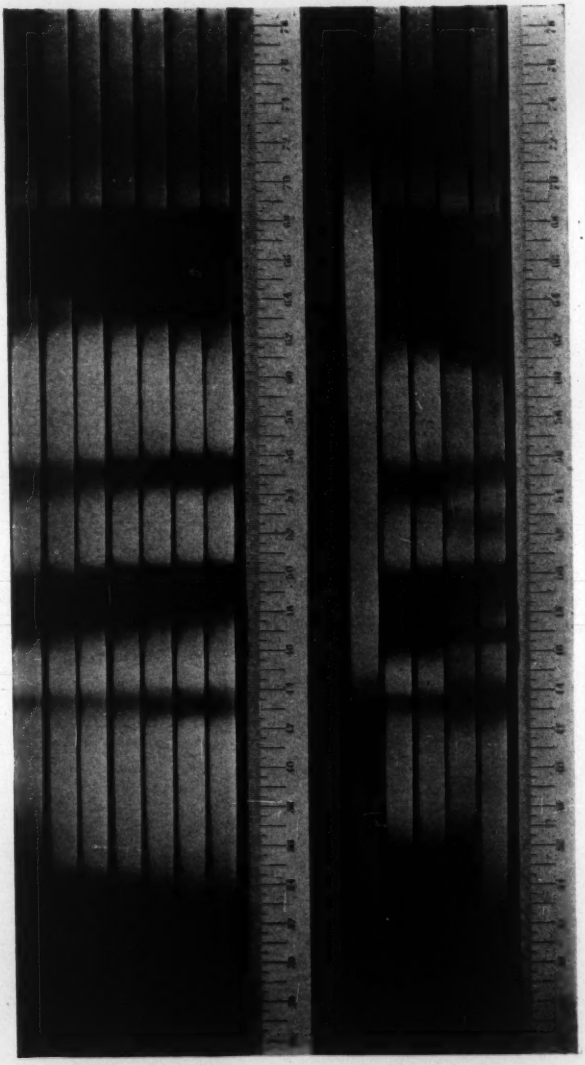
Neodymium Chloride in Ethyl Acetate and Anthracene

It was supposed by the older writers on the absorption spectra of solutions that if two colored salts were dissolved in the same solution the frequencies of the absorbing centers of the one salt would be modified by the presence of the other salt if the frequencies of the absorbing centers of the latter were almost the same as those of the former. Several attempts have been made to test this theory by experiment, but thus far no case has been found where such an effect is shown, at least by the inorganic salts.

According to our theory of aggregates we would hardly expect any two absorbing centers to have any mutual effects on each other unless both centers were part of the same aggregate. It is, however, quite difficult to find any solution containing such aggregates; indeed, it is doubtful it there are any that contain absorbing centers that have bands in the same region of the visible part of the spectrum. This line of work seems to be much more promising in the infrared.

It is known that, in the ultraviolet, anthracene and the neodymium salts have absorption bands that are near together. It was, therefore, hoped that a neodymium salt dissolved in anthracene would form aggregates containing both of these compounds, and that the resultant absorption spectrum would not be simply the superposition of the two separate absorption spectra of the given neodymium salt and anthracene. Unfortunately, the neodymium salts that were tried were not soluble in anthracene, and it seems, therefore, unlikely that we obtained aggregates containing both salts. Nevertheless, some spectrograms were taken with this idea in mind. Neodymium nitrate and anthracene are both soluble in ethyl acetate, and several solutions containing these three substances were prepared. It was found that only very dilute solutions of anthracene allowed the ultraviolet part of the spectrum to be transmitted, and no good photograph was obtained that showed the anthracene and neodymium nitrate ultraviolet bands. It would seem very doubtful that any effect would be obtained, because of the improbability of anthra-

Plate XI



A B

cene and neodymium nitrate being contained in the same aggregate.

It is hoped, however, that this effect can be satisfactorily tested with reference to the theory of aggregates, especially in the infrared.

The Uranyl and Uranous Bands

The uranyl bands are usually ten or twelve in number and, starting at about λ 5000, have been designated by the letters *a*, *b*, *c*, etc., and form a series, the head band being the *a* band. The uranous bands appear throughout the spectrum and do not form any series. The uranous bands are characteristic of the uranous salts, and spectrograms of the absorption spectra of a uranous salt gradually oxidized into a uranyl salt by the addition of hydrogen peroxide show the complete independence of the two spectra.

A problem of considerable interest, and one that seems capable of solution, is the complete correlation of the *a*, *b*, *c*, ... bands for the various uranyl salts in each solvent. For most solvents the uranyl bands of the different uranyl salts are very much alike. In aqueous solutions the differences are very marked, but by taking spectrophotographs of the transformation of one salt into another salt[1] we have succeeded in obtaining many relationships of this kind. By extending the work to low temperatures, and to the partly overlapping phosphorescent band spectra, it ought to be possible to connect continuously the various changes that these bands undergo.

Oxidation of Uranous to Uranyl Salts in Solution

Some spectrophotographs have been made of the formation of a uranous salt from a uranyl salt by reduction with nascent hydrogen. These spectrograms are somewhat unsatisfactory, since a considerable amount of gas, opaque residues, etc., is formed, and the reduction takes a considerable length of time. It is hoped in the future that this reduction may be produced by the action of occluded hydrogen (for example in palladium) that will be liberated on being heated, or by some other method that will not require the addition of foreign acids or salts.

[1] Publication 130, Carnegie Institution of Washington.

The reverse process of the oxidation of uranous salts in solution is a very satisfactory one, and the spectra can be photographed very well indeed. This method simply consists in the addition of a small amount of hydrogen peroxide to the uranous solution. The spectrophotography of these reactions, as already mentioned, has furnished an admirable method by means of which the uranyl and uranous bands can be completely separated. Several oxidizing agents have been added to aqueous and alcoholic solutions of uranous salts that showed both the water and alcohol bands in order to see whether there is any selective oxidation.

Oxidation of Uranous Chloride by Hydrogen Peroxide

In order to compare the effect of the presence of acids and of other salts, the intensely colored solution of uranous chloride formed by reducing an ether solution of uranyl chloride was the first to be oxidized. To one part of this solution were added four parts of water. It required for oxidation about one-fourth part of a solution of hydrogen peroxide. A cloudy and semitransparent precipitate was formed during oxidation. When one part of the ether solution of uranous chloride was added to six parts of concentrated hydrochloric acid, the resultant liquid contained a cloudy precipitate. The addition of a few drops of hydrogen peroxide clarified the solution, but it required over two parts of hydrogen peroxide before the uranous chloride was completely oxidized. Following are the tabulated results of these experiments:

Parts uranous chloride solution	Parts of solvent added	Parts hydrogen peroxide in water necessary for oxidation
1.0	4.0 water	0.6
1.0	6.0 HCl. Soluble	2.0
1.0	12.0 $AlCl_3$ in water. Small precipitate	0.7
1.0	6.0 conc. HNO_3. Only partly oxidized	3.0
1.0	10.0 acetic acid. Precipitate formed	0.7
1.0	12.0 ethyl alcohol	0.5
1.0	12.0 glycerol	0.7
1.0	12.0 methyl alcohol. Precipitate formed	0.6
1.0	12.0 $Ca(NO_3)_2$ in $2H_2O$ and $3CH_3OH$. Precipitate	0.4
1.0	90.0 ethyl alcohol	0.6
1.0	12.0 water, 4.0 $NaClO_4$ in water, and HCl	1.5

A solution of uranous chloride in water was prepared in the usual manner, and made strongly acid by the addition of hydrochloric acid, in order to increase its stability. Solutions of uranous salts sometimes form precipitates on standing. Uranous chloride was dissolved in the solvents, and mixed with the compounds indicated below:

Parts uranous chloride solution	Parts of solvent added	Parts of hydrogen peroxide necessary for oxidation	
1.0	10.0 water	0.2	
1.0	10.0 ethyl alcohol	0.2	
1.0	10.0 glycerol	0.35	
1.0	10.0 hot water	0.2	precipitated
1.0	10.0 water + H_2SO_4	0.1	
1.0	10.0 acetic acid	0.2	
1.0	10.0 acetone	0.2	precipitated
3.0	10.0 nitric acid	2.0	
1.0	10.0 calcium nitrate in $2H_2O$ + $3CH_3OH$	0.2	
1.0	10.0 hydrochloric acid	2.0	
1.0	10.0 aluminium chloride in water	0.25	
1.0	10.0 sodium perchlorate in water	0.2	
1.0	10.0 aluminium chloride in hot water	0.16	
1.0	7.0 hot hydrochloric acid	0.8	
3.0	8.0 hot nitric acid	0.0	NO_2 formed

A spectrogram was made showing the effect of the addition of hydrogen peroxide to an aqueous solution of uranous chloride of about 0.75 normal concentration. The uranous chloride solution did not show any uranyl bands at all, and even when the uranous bands appeared very strongly there was very little absorption in the region from λ 3500 to λ 4200. The edges of the uranous bands were well defined, there being four very strong bands extending between the following limits: λ 4250 to λ 4400, λ 4700 to about λ 5080, λ 5400 to λ 5600, and λ 6100 to λ 6800. The transmission between these bands was quite strong and appeared to be uniformly distributed.

The addition of hydrogen peroxide caused the uranous bands to decrease in intensity. As far as the quite sharp uranous bands are concerned it seems that the individuality

of these bands decreases at about the same rate; but the λ 4340 band is replaced by the blue-violet uranyl band, and the λ 5500 band is also apparently replaced by wide general absorption in this region, extending 500 or 600 Angström units. On the other hand, the transmission seems to be pretty complete in the red, and, with the exception of the very weak uranyl bands, in the region λ 4500.

A photograph showing the effect of the addition of hydrogen peroxide to a solution of uranous chloride in water, acetone and hydrochloric acid was taken. The solution did not contain the right proportion of the solvents to show the fine structure of the uranous and uranyl bands brought out by some acid acetone solutions. The spectrogram shows very clearly the various uranous bands, and how they are replaced by the uranyl bands as hydrogen peroxide is added.

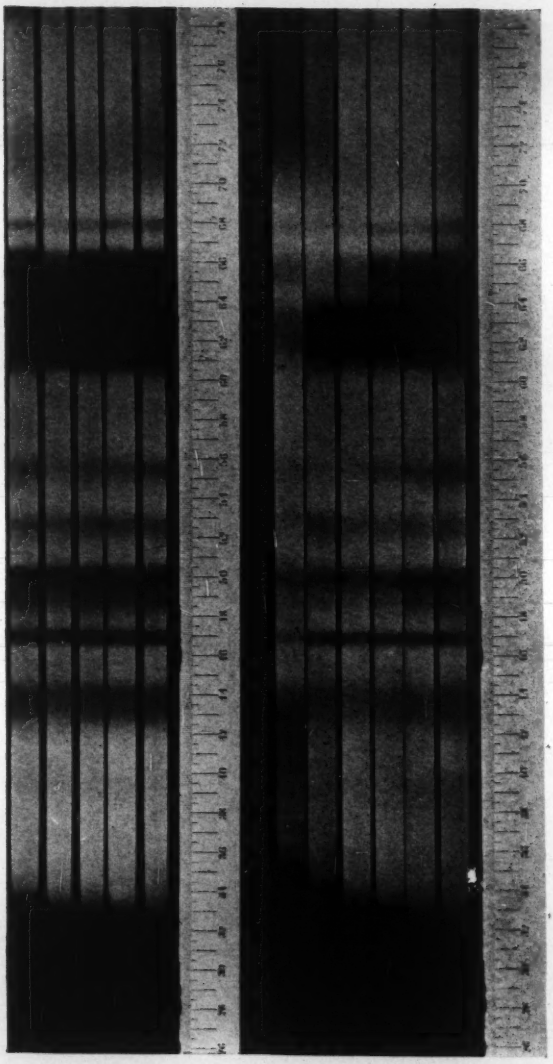
The band that appears at about λ 4970, and is quite strong on several of the strips, is a uranous band and disappears when sufficient hydrogen peroxide is added. In the strip which represents the absorption of the uranyl salt there is a wide, very diffuse and weak region of absorption, running from about λ 5000 to λ 5100.

In addition to the ordinary uranous and uranyl bands, there is a weak band about 15 Angström units wide at about λ 5080. This band appears best in the central strips, and can hardly be detected at all in the lowest and highest strips. It is, therefore, difficult to say whether it is a uranyl or a uranous band. In fact, it may not be due to either of the two uranium salts. The band is similar to the one described under the oxidation of uranous chloride in hydrochloric acid, with the exception that the bands have very different wave lengths.

Oxidation of Uranous Chloride in Hydrochloric Acid by Hydrogen Peroxide

It seems that the acid uranous aggregates are in general more stable than the neutral aggregates. Hydrogen peroxide oxidizes the strongest acid solutions. A spectrogram was, however, made of a neutral uranous chloride solution to

Plate XII



A B

which a large amount of concentrated hydrochloric acid had been added, and to which increasing amounts of hydrogen peroxide were added. The addition of the hydrochloric acid caused the uranous chloride bands to be shifted about 100 Angström units towards the red. In other respects the bands were not greatly changed, with the exception of the bands in the red.

The uranous bands, on the addition of hydrogen peroxide, gradually decreased in intensity without having their wave length changed. At the same time the uranyl bands appeared and, as is the case for strongly acid solutions, the uranyl bands appeared quite sharp and intense.

It may be supposed that in the case of the existence of acid aggregates it would require a longer time for the oxidation to take place than in the case where only neutral aggregates are present. It would be interesting to know what the reaction velocities of these oxidation reactions are for the various kinds of aggregates.

It is a difficult matter to preserve uranous nitrate in the uranous condition. When uranyl nitrate is mixed with nitric acid and zinc is added, some uranous nitrate is formed, but it is soon retransformed into the uranyl condition. This would indicate that uranous nitrate in water containing nitric acid is unstable and is quickly oxidized. On the other hand, uranous chloride can be mixed with concentrated nitric acid and the uranous absorption spectrum will be found to be entirely different from that of uranous chloride. In this case the uranous salt will remain as such for at least a day or two when kept at room temperatures. This may be explained by supposing that the nitric acid aggregate of uranous nitrate is much more stable than the salt itself.

According to the law of mass action, if a nitrate is mixed with uranous chloride, some uranous nitrate ought to be formed. To test the stability of uranous nitrate, uranous chloride was dissolved in a solution of calcium nitrate in water and methyl alcohol. Under these conditions both "water" and "alcohol" bands appeared. This solution did not oxidize, but a black precipitate was formed. This experiment could also be ex-

plained by supposing that the uranous nitrate in this solution existed in the condition of some kind of an aggregate. The precipitate formed appeared to be similar to that which is formed on heating a neutral uranous salt to the boiling-point.

Uranyl chloride, hydrochloric acid and potassium nitrate were mixed in water and methyl alcohol, and zinc was added. The reduction took place easily and the resulting uranous salt remained stable. It is probable that in this case, also, more stable aggregates than neutral uranous nitrate were formed. As a reciprocal reaction, uranyl nitrate, aluminium chloride and hydrochloric acid (in small quantity) were dissolved in water and zinc added. A stable solution of a uranous salt, probably largely chloride, was formed. In this case probably very little uranyl nitrate existed in the solution after the aluminium chloride and hydrochloric acid were added. These three experiments would then indicate that there is probably but little oxidation of uranous chloride to the uranyl salt under these conditions.

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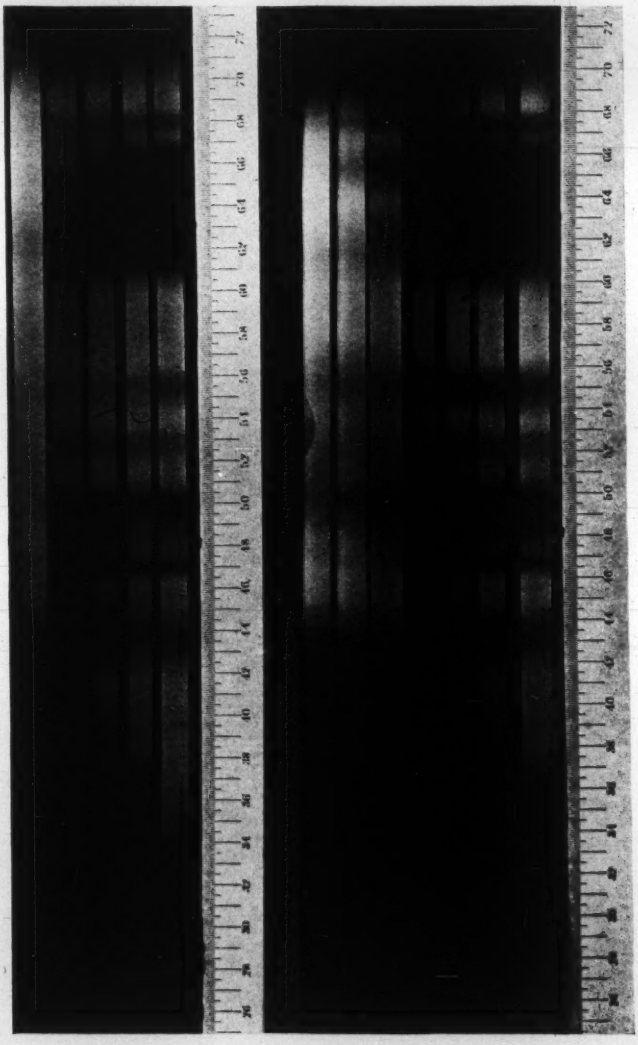
The Oxidation of Uranous Sulphate

The preparation of concentrated aqueous solutions of uranous chloride and uranous bromide is not difficult, the method of reduction of the corresponding uranyl salt with nascent hydrogen being used. A concentrated aqueous solution of uranous sulphate can be obtained in a similar manner, but on standing almost all of the uranium is precipitated. In the presence of sulphuric acid, however, a far more concentrated solution of uranous sulphate can be prepared, and this is quite stable.

A solution of uranous sulphate was prepared by reducing uranyl sulphate with nascent hydrogen. The precipitate formed was partly dissolved in water. The aqueous solution of uranous sulphate thus prepared was approximately 0.1 normal, and was fairly stable when kept in ground-glass stoppered bottles. When exposed to the air it oxidized slowly to the uranyl condition. The addition of methyl alcohol, ethyl alcohol or acetone to the aqueous solution of uranyl sulphate precipitated some of the salt.

Plate XIII



A B

A spectrogram was made showing the oxidation of an aqueous solution of uranous sulphate to uranyl sulphate by the addition of an aqueous solution of hydrogen peroxide.

The original film shows quite a large number of the uranyl bands. The wave lengths of the uranyl bands seem somewhat greater than those of uranyl sulphate solutions made from the chemically pure salt. This is probably due to the presence of a considerable amount of zinc sulphate. In addition to the regular uranyl sulphate bands there is present quite a fine and weak band at λ 5100. This band does not seem to vary to any considerable extent from strip to strip, and it is difficult to say whether it is a uranyl or a uranous band.

The Oxidation of Uranous Bromide by Hydrogen Peroxide

An aqueous solution of uranous bromide is oxidized by hydrogen peroxide in the same way that uranous chloride is oxidized. The absorption spectra of the bromide and chloride are quite similar for the uranyl and the uranous salts.

A solution of uranous bromide in ethyl alcohol is oxidized by hydrogen peroxide. In the case photographed the alcoholic solution had a very great ultraviolet, violet and blue absorption after the oxidation had taken place.

A photograph was taken showing the oxidation of a glycerol solution by the addition of hydrogen peroxide. In addition to a very few of the uranyl bands, the characteristic uranous glycerol bands consist of a wide diffuse band at λ 4400 and a strong and quite persistent band at λ 4680. This is about the most persistent band in the uranous spectrum, although in the lower strip it is only about 40 Angström units in width, while the red band is about ten times as wide. The bands $\lambda\lambda$ 4400, 5000 and 5250 are very much alike, being about 100 Angström units in width, very weak and diffuse. The band λ 5000 is apparently double. The red band is quite strong, running from λ 6050 to λ 6400. It is accompanied by a very weak band at λ 6600. This band is extremely weak, and probably corresponds to the water band in the same region. The addition of hydrogen peroxide simply causes each one of these bands to decrease in intensity, while the uranyl bands increase in intensity.

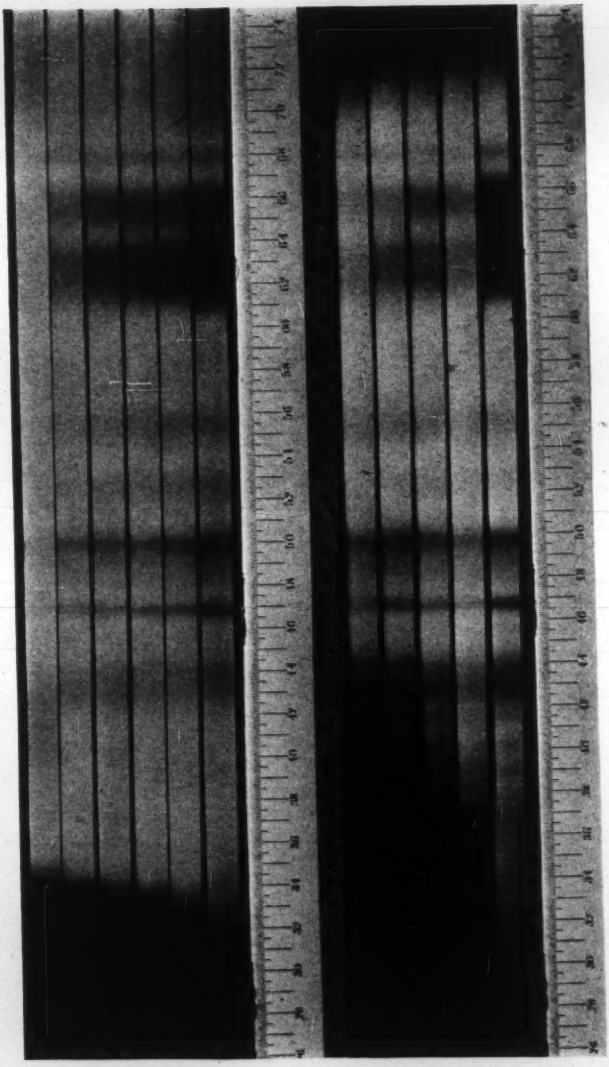
A Possible Method of Measuring the Strengths of Acids

Several methods have been employed for measuring the relative strengths of acids. Among these are: the power of acids to divide a base between them, as determined by thermochemical and volume-chemical methods; to invert cane sugar; to saponify an ester; to convert acetamide into ammonium acetate; their conductivity, etc. All of these methods measure the relative concentrations of the hydrogen ions in the solutions of the various acids, the degree of dissociation determining, of course, the relative strengths of acids. All acids at infinite dilution, or when completely dissociated, are, then, of the same strength. In more concentrated solutions the strengths of acids vary directly as their dissociation. Our work on absorption spectra has shown that the positions of the uranyl and the uranous bands for different uranium salts are often quite different. We could add just enough of the acid in question to transform completely the original salt into the salt of the acid in question, and then express the concentration of the acids and salts in gram molecules per liter, or by any other convenient method.

Some spectrograms of this kind have been made, indicating the relatively great strength of hydrochloric acid. As yet, however, the subject has only been touched upon. It is important that an accurate quantitative method for measuring the intensity and wave length of the bands be first devised. There will be one obstacle that may cause some difficulty in this method, and that is the presence of the acid (above, the acetic acid) displaced from the colored salt by the addition of the acid to be tested.

Experiments of this kind should be carried out with various uranyl, uranous and neodymium salts, etc., in different solvents, to find whether the relative strengths of acids are the same for the various colored salts, for the different solvents, for different concentrations, for different temperatures, for salts when in the presence of colorless salts, etc. Spectrophotography of this kind only includes a study of the spectra as they are changed from that of one neutral salt to that of another. Such a method, however, could hardly be made as

Plate XIV



A B

accurate a measure of the strength of acids as the conductivity method, and is not nearly so general.

Are the Ions Factors in the Absorption of Light?

One of the remarkable facts brought out in this investigation is that ions as such do not seem to play any role in the absorption of light. If the ions were the absorbers of light in solution, then the absorption spectrum of a solution should vary with the dilution of the solution, since the dissociation of a solution varies with the dilution.

There are solutions of the different colored salts of a certain metal for which the wave lengths of the absorption bands are different. It will be remembered in the case of neodymium that the absorption spectra of the acetate, chloride and nitrate are quite different from one another. The spectra of these salts should all be the same, in dilute solution, if the absorption of light were due solely to the ions.

Jones and Guy are now studying very dilute solutions of certain salts to see whether there is any detectable difference between the spectrograms of very dilute and of more concentrated solutions.

There are not very many cases known where the wave lengths of the absorption bands of different salts of the same metal in the same solvent are very different. Uranyl nitrate in water, however, gives bands that are of quite different wave lengths from those given by other uranyl salts in water. The following will illustrate this point:

	a	*b*	*c*	*d*	*e*	*f*
Uranyl nitrate	4870	4705	4550	....	4310	4155
Uranyl sulphate	4900	4740	4580	4460	4330	4200

While previous work of Jones and Strong[1] indicated that there was little or no change in the positions of the nitrate and sulphate bands with change in concentration, recent experiments made with the 0.5 and 0.003 normal solutions seem to show that in the more dilute solutions the sulphate bands have been slightly shifted towards the violet, while the nitrate bands have been slightly shifted towards the red. It may be

[1] P. Am. Phil. Soc., **48**, 192 (1909).

possible that, with sufficient dilution, the sulphate and nitrate bands would occupy the same position, as would be the case if the ions were the only absorbers in the solutions; yet the shifts are so small with the dilution that this seems improbable.

Indeed, it has recently been shown by Jones and Guy, working with very dilute solutions and with a depth of layer of 250 cm., that the uranyl nitrate bands are only very slightly shifted towards the red, and the uranyl sulphate bands only very slightly towards the violet. The evidence is therefore convincing that the presence of the NO_3 and the SO_4 groups influences the periods of the absorbing centers in the uranyl atoms or groups. Another good example that can be tested in a similar way is that of uranyl chloride and uranyl nitrate in acetone. These uranyl bands are quite strong, and the difference in wave lengths of corresponding bands is at least from 50 to 60 Angström units.

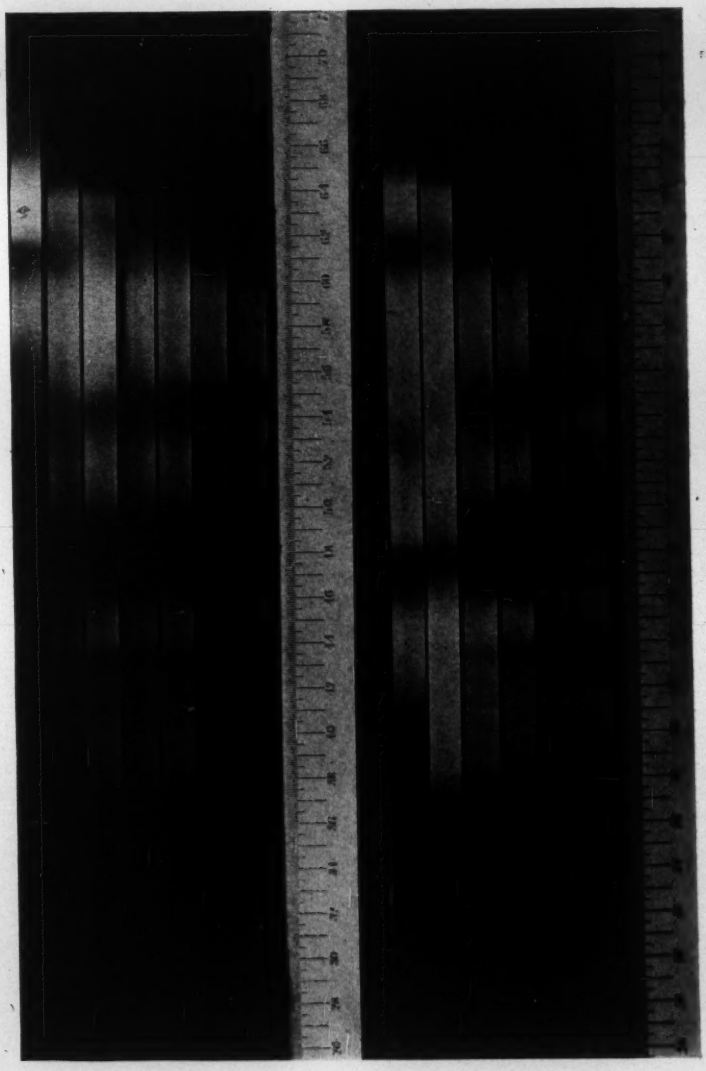
Uranyl nitrate in acetone	4840		4665		4515
Uranyl chloride in acetone	{4960 / 4935}	double	{4765 / 4795}	double	4610

Such facts as the above can be readily explained in terms of the theory of aggregates. A uranyl nitrate aggregate loses an NO_3 group, and becomes an ionized aggregate or complex ion. The loss of the NO_3 group causes a decrease in the hypsochromous effect, but this would be smaller if the aggregate were large. There would be a similar result in the case of the uranyl sulphate aggregates. It is, however, surprising that these aggregates, if they exist, are not broken up when the solution becomes very dilute.

It is important that acid aggregates should be studied in the same way. It is possible that these would break up more easily with increase in dilution than the neutral aggregates apparently do.

Work of Jones and Guy, carried out since the above was written, shows with certainty that the ions have different absorption from the molecules.

Plate XV



A B

The Oxidation of Uranous Salts by Nitric Acid

On account of the very great instability of uranous nitrate, it was expected that the addition of concentrated nitric acid to aqueous solutions of other uranous salts would cause their rapid oxidation. In the case of uranous bromide, bromine was given off. In general, the addition of nitric acid to an aqueous solution of uranous chloride causes the oxidation of that salt, but if a large amount of nitric acid is added the uranous chloride changes from a very deep green to a light greenish yellow, and the absorption spectrum shows that there is still a very considerable amount of uranous salt in the solution, and the bands are quite different from those of neutral uranous chloride. This uranous solution will remain for days, and seems to be quite stable.

A, Plate XV, represents the absorption of a solution of uranous bromide in water and methyl alcohol to which dilute nitric acid is added in increasing amounts. The addition of the nitric acid caused a slight increase in the transmission in the ultraviolet, but this was quite small. The uranyl bands appear, but are very weak. In Strip 1 there is a band running from λ 4200 to λ 4400. This is probably due to a water and alcohol band, the alcohol band being on the red side. Apparently the alcohol band disappears, since the band narrows rapidly on its red side, and then decreases slowly in intensity. The alcohol band at λ 4650 has practically disappeared in the third strip. In strip 1 there is a weak, very diffuse band at t 4800, and a strong band at about λ 4950. As nitric acid is added these bands are replaced by a wide and strong region of absorption, running from λ 4600 to λ 5000. The band λ 5200 disappears. The band λ 5500 is shifted about 150 Angström units towards the violet. The alcohol band running from about λ 6000 to λ 6300 narrows rapidly on its short wave-length edge, disappears, and is replaced by a weak, diffuse band at about λ 6100. The red water bands increase and then gradually decrease in intensity. When this decrease begins, the long wave-length band is much the stronger of the two and indicates that the uranous bromide alcoholate and the uranous bromide hydrate have both been changed

to some uranous nitrate hydrate, and that this compound is then oxidized to the uranyl salt.

The addition of nitric acid to the aqueous solution of uranous sulphate previously described produces a slow oxidation of the uranous into the uranyl salt. This oxidation requires several minutes, and would be a very good reaction with which to study reaction velocity, the intensity of the absorption band being determined by a radiomicrometric method. *B*, Plate XVI, is a spectrograph of the oxidation produced by adding nitric acid to an aqueous solution of uranous sulphate. Strip 5 represents the absorption of the same solution as that shown by Strip 4, the only difference being that the solution had been allowed to stand for several minutes.

In the solution of uranous sulphate oxidized by nitric acid, the uranyl bands are shifted slightly towards the violet, compared with the uranyl bands of the uranous sulphate solution oxidized by hydrogen peroxide, showing that probably some uranyl aggregate is formed that contains some NO_3 groups.

The addition of the first amount of nitric acid causes the transmission in the ultraviolet to be increased very greatly, with the appearance of a large number of the uranyl bands. In the red the wide uranous sulphate band is decreased in intensity. Strips 2 and 3 show the narrow red sulphate water band, but in Strip 4 this band has completely disappeared and is replaced by a single weak band 300 Angström units wide.

B, Plate XV, represents the change in the absorption spectrum of a solution of uranous chloride in alcohol and acetone, to which nitric acid is added. This spectrogram shows the rapid disappearance of the alcohol bands. The various uranous bands seem to be replaced by the bands of some hydrate of a uranous nitrate aggregate, and this aggregate is then gradually oxidized. The ultraviolet transmission increases until the last strip, which shows a very great increase in the ultraviolet absorption. The last strip still shows the presence of a considerable amount of uranous salt, and the absorption bands are entirely new.

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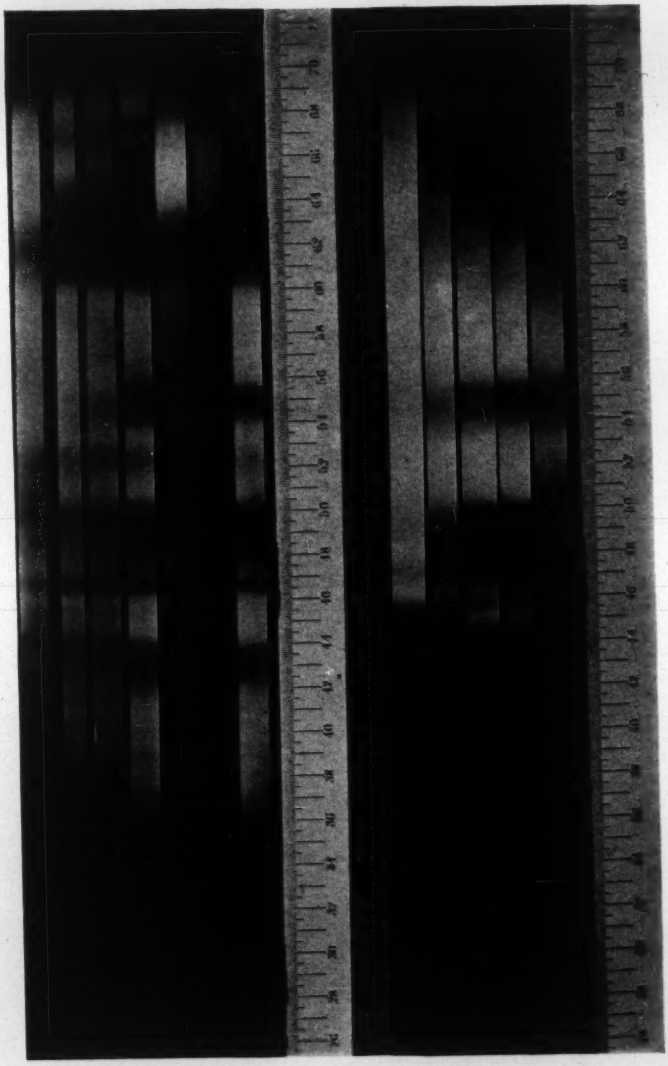
Plate XVI



A B

A, Plate XI, represents the absorption spectrum of uranous chloride as it is gradually changed into uranous nitrate by the addition of nitric acid. *B*, Plate XI, represents the corresponding changes in the absorption spectra that take place when to a solution of uranous chloride in equal parts of water and methyl alcohol is added nitric acid, also dissolved in equal parts of water and methyl alcohol. The upper strip represents the absorption of the resultant uranyl salt after oxidation with hydrogen peroxide. As the bands are quite wide and strong most of the changes can be seen on the plate itself. It will be seen that the absorption spectrum of the nitric acid solution of uranous chloride is very different from that of the neutral chloride. This spectrogram also seems to indicate that there is not a gradual shifting of the chloride bands into the nitrate bands, but in the case of the λ 6300 chloride band there is a decrease in intensity without any shift, and this is replaced by the uranous nitrate band at about λ 6100. *B* shows that the addition of nitric acid results in a rapid and almost *complete disappearance of the alcohol bands, while the uranous nitrate water bands increase in intensity.*

Uranous Acetate and the Effect of the Addition of Nitric Acid

The reduction of uranyl acetate to the uranous salt is not complete, and a precipitate was formed, so that the resultant solution here used was quite dilute. A spectrogram was made of this solution. The addition of nitric acid causes a great increase in the general transmission throughout the spectrum and a very rapid decrease in the intensity of the uranous bands. The resultant uranous bands are, of course, those of uranous nitrate. This spectrogram shows that uranous acetate is quickly oxidized in the presence of nitric acid, whereas this is not the case with uranous chloride.

The Selective Action of Chemical Reagents on Solvates

After photographing the effect of oxidizing the uranous salts to the uranyl condition by the addition of hydrogen peroxide, it was natural to study what effect the addition of other oxidizing agents would have upon the various solvate bands. It will be remembered that the addition of hydrogen

peroxide caused the complete oxidation of the various solvates in the solution. It was found that the action of the other oxidizing agents used was, in general, of a more or less selective nature.

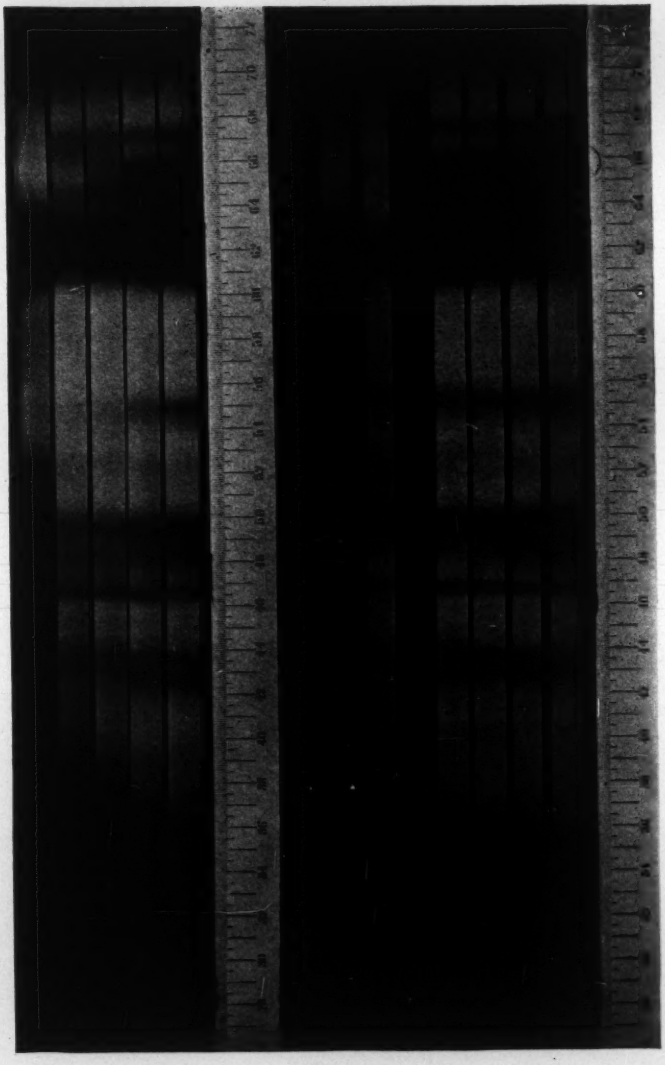
A, Plate XVII, represents the absorption of a solution of uranous bromide in 3.5 parts water and 6 parts methyl alcohol, to which was added a 1.2 normal solution of calcium nitrate in methyl alcohol.

	Drops of calcium nitrate in methyl alcohol	Percentage water in solution
Strip 1	0	37
Strip 2	10	33
Strip 3	20	28
Strip 4	40	21
Strip 5	80	14

The addition of calcium nitrate causes a very great increase in the amount of the general absorption of the short wave lengths. This is to be especially noticed in the last addition of the calcium nitrate. The most important thing to be seen from this spectrogram is the rapid and almost total disappearance of the water bands. The intensity of the alcohol band changes very little, if any, and it seems quite improbable that the uranous hydrate could have been converted into uranous alcoholate without the alcohol bands increasing very much in intensity. The natural conclusion is that the uranous hydrate has been oxidized to the uranyl condition by the calcium nitrate. The original film shows that in the third strip the two red uranous water bands have almost the same intensity. This may mean that the uranous bromide has been changed to some other salt.

B, Plate XVII, represents the absorption of a solution of uranous bromide in 4 parts of water and 6 parts of methyl alcohol, the resultant solution being about 0.12 normal. To this were added small amounts of a solution of sodium perchlorate in methyl alcohol. It will be seen that the water bands decrease in intensity as the sodium perchlorate is added, and that the longest wave-length water band becomes more diffuse. The reason why the fifth strip is vacant is on account

Plate XVII



A B

of the formation of a precipitate. The precipitate was not analyzed, but the spectrogram shows that the uranous hydrate has almost entirely disappeared from the solution, while there is still present quite a considerable amount of uranous alcoholate. This spectrogram is, therefore, a good example of a case of *selective precipitation of solvates*. *B*, like *A*, Plate XVII, indicates that there is a change in the constitution of the uranous hydrate before it was precipitated.

A, Plate XVI, represents the effect of the addition of potassium nitrate and calcium nitrate to a solution of uranous bromide. In Strip 1 we have the absorption due to a solution of uranous bromide in 3.5 parts water and 6 parts methyl alcohol. To this is added a solution of potassium nitrate in 4 parts water and 6 parts methyl alcohol, a precipitate being formed. The precipitate was filtered off and the resultant solution gives the absorption as represented in Strips 2 and 3. It will be seen that only the uranous hydrate has been precipitated. Strip 4 represents another solution of uranous bromide in 3.5 parts of water and 6 parts of methyl alcohol, to which is added calcium nitrate dissolved in 4 parts of water and 6 parts of methyl alcohol. The effect of the addition of this calcium nitrate is to cause the almost complete disappearance of the water bands, while the intensity of the alcohol bands remains practically the same. In the fifth strip it will be seen that the long wave-length water band is nearly 150 Angström units in width, and is very much wider than the other red water band. This spectrogram furnishes striking evidence in support of the view of the selective oxidation of the uranous hydrate in this solution.

A photograph representing the absorption of uranous bromide in water and methyl alcohol to which an aqueous solution of calcium nitrate is added was taken. This spectrogram shows the decrease in the intensity of the alcohol bands. This is most likely due to the increase in the percentage of water present in the solution. The second strip shows the very quick change in the relative intensity of the two red uranous water bands. This effect seems to be a general one for the addition of calcium nitrate to solutions of uranous chloride,

bromide or sulphate. The spectrogram does not seem to indicate that any of the uranous salt has been oxidized.

B, Plate XIII, shows that when hydrogen peroxide is dissolved in the same proportion of water and methyl alcohol as the uranous bromide, the alcohol and water bands both disappear at the same rate, indicating that hydrogen peroxide has no selective action on these two solvates.

The solution of uranous chloride used was acidulated with hydrochloric acid, and when mixed with an equal volume of methyl alcohol it gave the water and methyl alcohol bands of about the same intensity. Two solutions were used, one in which the alcohol bands were much the stronger, and the other (*A*, Plate XIII) in which the water bands were slightly stronger. Calcium nitrate in 2 parts of water and 3 parts alcohol was added, the amounts being 10, 20, 40 and about 120 drops. The last strip of *A*, Plate XIII, represents the result of the addition of hydrogen peroxide. *A*, Plate XII, represents the effect produced by adding sodium perchlorate dissolved in equal parts of water and alcohol. In this case no oxidation resulted. The spectrogram shows very little change in either the water or the alcohol bands. The red water bands have their relative intensity greatly changed, however, on the addition of calcium nitrate. *A*, Plate XIII, illustrates this same relative change in the intensity of the two red water bands. The spectrogram shows a very considerable increase in the intensity of the alcohol bands, and a decrease in the intensity of the water bands. *A*, Plate XII, shows very little if any change at all in the absorption spectra. Even the red water bands remain of about the same relative intensity.

B, Plate XII, represents the absorption of one part of uranous chloride in water to which one part of methyl alcohol is added. Succeeding strips, with the exception of the last, show the effect of adding potassium chlorate in water and methyl alcohol. The last strip represents the effect of adding hydrogen peroxide. This spectrogram shows the almost complete disappearance of the water bands, while the alcohol bands remain of about the same intensity.

Plate XIV, *A*, represents the absorption of uranous chloride

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Plate XVIII

A B

in one part of water and one part of methyl alcohol. Hydrogen peroxide, in equal volumes of water and methyl alcohol, was added to this solution, three drops at a time; except to the solution whose spectrogram is shown in the last strip, twelve drops of hydrogen dioxide were added. The uranous alcoholate and hydrate are oxidized to the same extent.

Plate XIV, *B*, shows the absorption due to 0.5 normal uranous bromide in water, to which three parts of methyl alcohol were added. After a time a precipitate was formed. This was filtered off, and Strip 2 is the spectrogram of the solution. Successive strips represent the effect of adding increasing amounts of potassium chlorate in equal volumes of water and methyl alcohol. Very little, if any, selective action manifests itself.

A, Plate VI, gives the absorption of concentrated nitric acid to which increasing amounts of uranous chloride were added.

B, Plate VI, represents the absorption of the filtrate of a uranous bromide solution. A solution of uranous bromide of sufficient strength, when mixed with alcohol, to give the water and alcohol bands of the same intensity usually forms a precipitate if allowed to stand. Strip 1 shows the absorption of the filtrate from such a precipitate and indicates the selective precipitation of the hydrate. The succeeding strips give the absorption of uranous bromide in water and alcohol to which is added nitric acid in the same proportion of water and alcohol. The last strip represents the solution containing the greatest amount of nitric acid to which is added a few drops of hydrogen peroxide.

C, Plate VI, shows the absorption of uranous chloride in propyl alcohol to which acetone is added. *A* gives what we shall call the uranous nitrate spectrum, although it is probably quite different from that of a neutral aqueous uranous nitrate absorption spectrum. *B* is a good example of selective precipitation and of the action of nitric acid in increasing the intensity of the hydrate bands at the expense of the alcoholate bands. *C* shows how the addition of acetone causes the almost complete disappearance of the uranous bands and how,

at the same time, the uranyl acetone bands appear in place of the uranous bands.

The Reduction of Uranyl Salts in Solution

The reduction of uranyl to uranous salts deserves a thorough study and undoubtedly offers a fertile field for investigation, and this partly on account of the light that quantitative spectrophotography will probably throw upon the subject. In certain solvents some interesting results have already been obtained. In the case of an ether solution of uranyl chloride it was found that, on the addition of zinc and hydrochloric acid, three phases resulted—an oily and extremely concentrated solution of uranous chloride formed at the bottom; a much more dilute solution of uranous chloride which was above the oily layer and which, on standing, gave up its uranous salt to the oily liquid below; and the upper layer, which contained only uranyl chloride in solution. These three liquid layers were completely separate from one another. When the whole system was thoroughly shaken and allowed to stand, the three strata soon separated again from one another.

Uranyl chloride dissolved in isobutyl alcohol to which zinc and strong hydrochloric acid are added also shows the formation of an oily and dense liquid, which was almost opaque on account of the large amount of uranous chloride dissolved in it. These very concentrated solutions of uranous salts would serve admirably for low-temperature work and for the detection of the Zeeman effect.

When hydrochloric acid is added to a solution of uranyl chloride in propyl alcohol, the two solutions mix. Zinc is then added and the reduction takes place very slowly.

B, Plate V, represents the absorption spectrum of the uranous chloride solution in ether to which some hydrochloric acid had been added. The absorption spectrum is quite characteristic, and shows some new bands. Several of these bands are quite sharp and narrow. As an example, there is a band near λ 5000 that is quite strong and is only about 25 Angström units in width.

Reduction of Uranyl Chloride in Methyl Acetate

To a solution of uranyl chloride in methyl acetate were added hydrochloric acid and metallic zinc. The hydrochloric acid does not mix with the acetate solution. For a considerable time hydrogen is given off, the acetate solution remaining of a greenish yellow color. Quite suddenly, however, the acetate loses its greenish yellow color and becomes slightly clouded, the solution being of a pale white color. At the same time there is formed an almost black solution whose volume is about the same as that of the hydrochloric acid added. Further addition of hydrochloric acid results in the acetate solution becoming of a dark green color, while a small amount of the very deeply colored, oillike solution still remained at the bottom of the solution.

Selective Reduction of Uranyl Aggregates

The method employed for the preparation of uranous salts for work on their absorption spectra has usually been to add an acid corresponding to that of the uranyl salt and some zinc. There would be present in the solution of the uranous salt the corresponding zinc salt. It is possible, under these conditions, to obtain fairly concentrated solutions of uranous chloride, uranous bromide and uranous sulphate. It does not seem, by this method, to be possible to obtain uranous nitrate in stable condition, as would be expected. A small amount of uranous nitrate is formed, but it is very quickly oxidized again. Dilute aqueous solutions of uranous acetate can be obtained by this method.

The most concentrated solution of any uranous salt thus far obtained is that of uranous chloride. A considerable volume of a solution of uranyl chloride in ether was prepared; to this was added a small amount of concentrated hydrochloric acid and zinc. The uranous chloride formed is nearly insoluble in the ether, and collects in a dark, oily liquid at the bottom of the vessel.

The action of certain acids on the uranyl salts is peculiar. As has been stated, the addition of nitric acid and zinc to a uranyl chloride solution did not result in the formation of any

uranous salt, although the absorption spectra would probably have shown very little effect on the uranyl chloride bands produced by the addition of nitric acid. The sulphate would probably have been a better uranyl salt to use in this connection, because the uranyl sulphate bands are harder to change to the nitrate bands than are the uranyl chloride bands. To a uranyl chloride solution containing some free hydrochloric acid was then added, as before, some nitric acid and zinc. In this case some uranous salt was produced, but it was quite unstable and was quickly oxidized again.

On the other hand, to an aqueous solution of uranyl chloride was added some hydrochloric acid and zinc. A uranous salt was formed, but in a few minutes this was transformed back into the uranyl condition again. This is rather unexpected, since the uranous salt is in the condition of the chloride, and the chloride is quite stable. To an aqueous uranyl nitrate solution was then added a large amount of concentrated hydrochloric acid and a little zinc. The solution turns green during the first few minutes and then goes over to the uranyl state, although hydrogen gas is being rapidly evolved. Very little could be done with the bromides along this line, on account of the liberation of bromine. It would be very interesting to find how much the uranyl bromide bands are changed before the bromine gas is evolved, since this would give the condition of the aggregate when it is broken up and bromine evolved.

DESCRIPTION OF PLATES

With the exception of the plates representing changes in temperature of the solution, the times of exposure and the width of the slit are the same for each strip of the plate. The current through the Nernst glower was kept constant. In the case of the uranyl salts a much longer exposure was often made in the ultraviolet and violet, in order to bring out the uranyl bands as strongly as possible, and this will be noted in the description. In some strips ultraviolet wave-length spark lines will be found, these being photographed without the solution in the path of light, and only for purposes of measurement. In exposures to the spark of this kind, the film holder was never moved between the photographing of the absorption spectra of the solution and that of the spark spectra. In some instances the strips are not uniformly exposed. This was due in many cases to the formation of precipitates. A great deal of trouble of this kind was encountered, especially with the uranous salts, in the high tem-

perature work, and in the spectrophotography of chemical reactions. In referring to the strips, the first or lowest strip is that at the bottom of the plate—the one that is nearest the scale of wave lengths. The scale of wave lengths is in Angström units, the whole number standing for so many hundred Angström units.

Plate I. *A.* Neodymium Chloride in Isopropyl Alcohol. Depth of cell, 30 mm. Concentration, 0.0266 normal.

B. Neodymium Nitrate in Tertiary Butyl Alcohol. Concentration, 0.2 normal.

C. Neodymium Chloride in Water and Alcohol. The lower strip represents about 8 per cent. water and shows both sets of bands. Concentration, 0.5 normal. The other strips show the effect of adding hydrogen peroxide.

Plate II. *A.* Neodymium Nitrate in Butyl and Isobutyl Alcohols. Strip 1 is a 3 mm. and Strip 2 a 13 mm. layer of a 0.3 normal solution in butyl alcohol; Strip 3 is a 3 mm. and Strip 4 a 13 mm. layer of a 0.6 normal solution in isopropyl alcohol.

B. Neodymium Nitrate in Mixtures of Ethyl and Isobutyl Alcohols. Depth of cell constant, 34 mm. Concentration constant, 0.1 normal. Starting with the lowest strip the percentages of the solvents were:

Ethyl alcohol	20	40	60	80	100
Isobutyl alcohol	80	60	40	20	0

Plate III. *A.* Uranyl Nitrate in Nitric Acid to which Increasing Amounts of Hydrochloric Acid are Added.

B. Uranyl Nitrate in Water to which an Aqueous Solution of Aluminium Chloride is Added. This spectrogram shows very clearly the shift of the uranyl bands towards the red.

Plate IV. *A.* Uranous Bromide in Water to which Methyl Alcohol is Added. This spectrogram shows the great difference between the water and methyl alcohol bands of uranous bromide.

B. Uranous Chloride in Water to which Methyl Alcohol is Added. The methyl alcohol was added in smaller quantities than to the solutions whose spectrograms are recorded in the above plate.

Plate V. *A.* Uranous Chloride in Ether. Depth of cell variable.

B. Uranous Chloride in Acetone. Depth of cell variable.

Plate VI. *A.* Uranous Chloride in Concentrated Nitric Acid. The uranous chloride is added to the acid which was placed in the Uhler cell. It is very remarkable that the uranous salt is not oxidized under these conditions.

B. Uranous Bromide in Water and Methyl Alcohol after the Precipitate has been Filtered Off (Strip 1). This shows a selective precipitation of the hydrate. The succeeding strips show the absorption of uranous bromide in water and methyl alcohol to which increasing amounts of nitric acid (in the same proportion of water and alcohol) are added.

C. Uranous Chloride in Propyl Alcohol to which Acetone is Gradually Added.

Plate VII. *A.* Dysprosium Chloride in Methyl Alcohol. Concentration about normal. In all the spectrograms of gadolinium, dysprosium and samarium, the slit width was 0.10 mm., the current in the Nernst glower 0.9 ampere, and the length of exposure 1 minute to the visible portion of the Nernst glower spectrum and about 5 minutes to the ultraviolet part of the Nernst glower spectrum. The depths of cell were 1, 5, 12, 20, 31 and 31 mm. The upper strip was exposed directly to the ultraviolet spark lines.

B. Dysprosium Chloride in Water. Concentration, 1.86 normal. Depths of cell, starting with lowest strip, 2, 6, 20, 15, 21 and 100 mm. All the strips except the lowest one were exposed directly to the ultraviolet spark lines.

Plate VIII. *A.* Dysprosium Acetate in Water. Concentration, 0.4 normal. Depths of cell starting with lowest strip, 4, 16, 25 and 34 mm. Exposures were made in Strips 2, 3 and 5 directly to the ultraviolet spark lines.

B. Dysprosium Chloride in Ethyl Alcohol. Concentration, 0.74 normal. Depths of cell, 2, 10, 15, 24, 30 and 30 mm. The upper strip was exposed directly to the ultraviolet spark lines.

Plate IX. *A.* Samarium Chloride in Water. Concentration, 1.31 normal. Depths of cell, starting with lowest strip, 2, 6, 12, 16, 20 and 100 mm. Strips 3, 4, 5 and 6 were exposed directly to the ultraviolet spark lines.

B. Samarium Chloride in Methyl Alcohol. Concentration about normal. Depths of cell 2, 5, 9, 18, 27 and 27 mm. The upper strip was exposed directly to the ultraviolet spark lines.

Plate X. *A.* Samarium Chloride in Ethyl Alcohol. Concentration, 0.9 normal. Depths of cell, 1, 4 9, 18, 25 and 25 mm. The upper strip was exposed directly to the ultraviolet spark lines.

B. Samarium Chloride in Ethyl Alcohol to which Water is Added. The first strip represents the absorption

of a 0.09 normal solution in ethyl alcohol. Succeeding strips represent the absorption of the same solution to which small quantities of water have been added. Starting with the lowest strip the depths of cell were: 18, 19, 20, 21.5, 22.5, 25 and 28 mm.

Plate XI. *A*. Uranous Chloride in Water to which Increasing Amounts of Nitric Acid are Added. The first strip was accidentally exposed a short time directly to the Nernst glower. This is a spectrophotograph of the chemical reaction of uranous chloride being converted into uranous nitrate.

B. Uranous Chloride in Equal Parts of Water and Methyl Alcohol (Strip 1) to which Nitric Acid (Strips 2, 3 and 4) and Hydrogen Peroxide (Strip 5) is Added. This spectrogram shows how the water and alcohol bands of uranous chloride are changed to the nitrate bands, and how these in turn are replaced by the uranyl nitrate bands. The uranous nitrate bands are seen to be very different from the chloride bands.

Plate XII. *A*. Uranous Chloride in Equal Parts by Volume of Water and Methyl Alcohol (Strip 1) to which are Added Increasing Amounts of Sodium Chlorate Dissolved in Equal Volumes of Water and Methyl Alcohol (Succeeding Strips). This spectrogram shows very little, if any, selective action on the uranous chloride water and alcohol bands.

B. Uranous Chloride in Equal Volumes of Water and Methyl Alcohol (Strip 1) to which Potassium Chlorate in Water and Methyl Alcohol is Added in Increasing Amounts (Strips 2, 3, 4 and 5), and to which Hydrogen Peroxide is Added in Addition (Strip 6). This spectrogram shows the selective action of potassium chlorate on the uranous chloride water and methyl alcohol bands. The water bands are seen to decrease in intensity, while the alcohol bands increase in intensity. In this example the addition of hydrogen peroxide seems to have oxidized only the alcoholated uranous chloride.

Plate XIII. *A*. Uranous Chloride in Water and Methyl Alcohol (Strip 1) to which are Added Increasing Amounts of Calcium Nitrate in 2 parts Water and 3 parts Methyl Alcohol (Strips 2, 3 and 4), and finally Hydrogen Peroxide (Strip 5). The spectrogram shows that the original solution was almost entirely free from uranyl chloride and that the addition of calcium nitrate had a marked selective action on the uranous bands, the water

bands being greatly decreased in intensity while the alcohol bands became more intense. The addition of hydrogen peroxide causes the complete disappearance of the uranous bands and the appearance of the uranyl bands.

B. Uranous Bromide in 2 parts of Water and 3 parts of Methyl Alcohol (Strip 1) to which Hydrogen Peroxide (2 parts of a 3 per cent. Hydrogen Peroxide Solution in Water with 3 parts of Methyl Alcohol) was Added 5 Drops at a Time (Strips 2, 3, 4, 5, 6 and 7). Strip 1 shows that the oxidation of the uranous chloride by the hydrogen peroxide is the same, as indicated either by the intensity of the water bands or the alcohol bands.

Plate XIV. *A*. Uranous Chloride in Water and Methyl Alcohol to which Hydrogen Peroxide is Gradually Added. This spectrogram shows the simultaneous oxidation of the hydrate and alcoholate of uranous chloride.

B. Uranous Bromide in Water and Methyl Alcohol to which Potassium Chlorate in Water and Methyl Alcohol was Gradually Added.

Plate XV. *A*. Uranous Bromide in Water and Methyl Alcohol to which Nitric Acid is Added.

B. Uranous Chloride in Acetone and Methyl Alcohol to which Nitric Acid is Added.

Plate XVI. *A*. Uranous Bromide in 7 parts of Water and 12 parts of Methyl Alcohol (Strip 1) to which is added Potassium Nitrate in 2 parts of Water and 3 parts of Methyl Alcohol (Strips 2 and 3), and Corresponding Strips (4, 5 and 6) where Calcium Nitrate is Added instead of Potassium Nitrate. The spectrogram shows the selective action of these salts on the water and alcohol bands, the water bands having practically disappeared in Strips 3 and 6.

B. Uranous Sulphate in Water to which Nitric Acid is Added in Increasing Amounts.

Plate XVII. *A*. Uranous Bromide in 7 parts of Water and 12 parts of Methyl Alcohol to which Increasing Amounts of Calcium Nitrate in Methyl Alcohol are Added.

B. Uranous Bromide in 2 parts of Water and 3 parts of Methyl Alcohol to which Increasing Amounts of Sodium Perchlorate in Methyl Alcohol are Added. These strips of *A* and *B* show the selective action of the calium nitrate and sodium perchlorate on the water and alcohol bands, the water bands practically disap-

pearing. In this case part of the effect may be due to the increased percentage of alcohol present.

Plate XVIII. *A*. Uranous Bromide in Water and Methyl Alcohol.

B. The First Three Strips Represent the Oxidation of an Aqueous Solution of Uranous Sulphate by Hydrogen Peroxide. The Other Four Strips Represent the Oxidation of a Sulphuric Acid Solution of Uranous Sulphate by Hydrogen Peroxide.

[*The second part of this paper will be published in the February number.*]

REVIEWS.

INTRODUCTION À L'ÉTUDE DE LA SPECTROCHIMIE. PAR G. URBAIN, Professeur de Chimie à la Sorbonne. Avec 70 figures dans le texte et 9 planches. Leçons professées à la faculté des sciences à l'université de Paris. Paris: Librairie scientifique A. Hermann et Fils. 1911. pp. iii + 248. Price, Fr. 10.

This book is a well-planned treatment of the spectroscopy of inorganic compounds, especially of solids and liquids. Some parts, especially the chapter on phosphorescence, contain new work recently done by the author.

The book is a collection of lectures which the author gives to students that are taking up the subject of spectroscopy. For this reason it contains practically no tables and is not intended for use in the laboratory as a book of reference. Neither is the book planned for carrying out analyses but to give the student a clear and exact account of our knowledge of inorganic spectroscopy. The style is clear and is typically French. The latest theories and discoveries are treated.

The seven chapters treat of the following subjects: Chapter one takes up the dispersion of prisms. This chapter should have included a discussion of gratings, especially as the small concave grating promises to come into general use. Flames are then treated. A description of Lenard's work should have been included. Stark's and Thomson's work on canal and positive rays should have been discussed in the following chapter on vacuum tubes. This work, although not having a direct bearing on the subject, is of such great theoretical interest and promises to open up such an important field of knowledge of the kinetics of chemical reactions that all works on theoretical spectroscopy or chemistry should include it. The spectroscopy of gases, especially those of the helium family, should have been treated. The chapters on the electric spark and phosphorescence are excellent, as are the last chapters on absorption and the constitution of complex spectra. At the

end of the book are nine plates of various kinds of spectra. These should have wave-length scales attached to them.

On the whole the work is a most excellent one and is exactly what its title claims. It is without doubt the best book of its kind that has been published. W. W. STRONG.

CHEMIE DER EIWEISSKÖRPER. Von DR. OTTO CONHEIM, a. o. Professor der Physiologie an der Universität Heidelberg. Dritte, vollständig neu bearbeitete Auflage. Braunschweig: Friedr. Vieweg & Sohn. 1911. S. xii + 388. Preis: geh., M. 11; geb., M. 12.

The appearance of the third edition of this excellent book will be welcomed by biological chemists. Although there have been no fundamental changes in our conception of the proteins since the last edition of this work, the application of modern methods to the study of a large number of proteins by many workers has led to a great increase in our knowledge of these substances. The general style of the work is the same as that of the last edition. The plant proteins receive a much more satisfactory treatment than in the last edition. The literature is brought up to the end of 1910. This work should be available to all chemists who are concerned with the biological aspect of their subject. A. S. L.

GRUNDRISS DER ANORGANISCHEN CHEMIE. Von Prof. Carl Oppenheimer, Dr. phil. et med. Berlin. Sechste Auflage. Leipzig: Verlag von Georg Thieme. 1910. pp. vii + 171. Price, M. 3.50.

This work, whose success is evident from the fact that the present is the sixth edition, is similar to the "quiz compends" which are so popular among medical students. It attempts to cover the whole field of inorganic chemistry, but can give, in the brief space available, only very condensed statements regarding the preparation and properties of inorganic substances. For example, even with the small size of the printed page, $6 \times 3^1/_2$ inches, only $2^1/_4$ pages are devoted to hydrogen, 1 to chlorine, $1^1/_2$ to oxygen, 2 to water, $^1/_2$ to air, etc. As the author states in the preface, this book is intended for pharmaceutical and medical students, architects, etc. To one who wishes some knowledge of the science of chemistry, and not simply a statement of facts, this book will prove of little value. J. E. G.

KURZE ANLEITUNG ZUR MASSANALYSE mit spezieller Berücksichtigung der Vorschriften des Arzneibuches und des Ergänzungsbuches. Bearbeitet von DR. LUDWIG MEDICUS, Professor an der Universität Würzburg. Mit 7 Abbildungen im Text. Neunte und zehnte, verbesserte und vermehrte Auflage. Tübingen: Verlag der H. Laupp'schen Buchhandlung. 1911. S. xv + 210. Preis: geh., 2.40; geb., M. 3.20.

This edition of the "Introduction to Volumetric Analysis"

differs from earlier editions only in certain methods revised or introduced because of changes in the "Arzneibuch." Little attention is given to the theoretical side of the subject so that the book is essentially a set of directions with the method of calculating results given for each analysis. The work is intended primarily for German pharmacists and follows so literally the books on which it is based that it is of little use to the general analyst and of doubtful value for the American pharmaceutical chemist.

R. S. WILLIAMS.

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS, or the Quantitative Determination of Chemical Substances by Measure, Applied to Liquids, Solids and Gases, Adapted to the Requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, etc., and for the Valuation of Substances used in Commerce, Agriculture and the Arts. By FRANCIS SUTTON, F.I.C., F.C.S., Public Analyst for the County of Norfolk, etc. Tenth Edition, Revised Throughout, with Numerous Additions, by W. LINCOLNE SUTTON, F.I.C., Public Analyst for the County of Suffolk, Norwich, Ipswich, etc., and ALFRED E. JOHNSON, B.Sc. Lond., F.I.C., A.R.C.Sc.I. Philadelphia: P. Blakiston's Son & Co. 1911. pp. xiv + 621. Price, $5.50.

The fact that the ninth edition has been out of print for more than eighteen months is an indication of the demand for this standard work on Volumetric Analysis, the general plan of which is so well known that it needs no comment. The tenth edition is like its predecessors in form and style but has been thoroughly revised by its junior editors to whom the author gives full credit for the numerous changes. Many of the older methods have been omitted and a number of new ones added. The sections on the calibration of measuring flasks, weights, etc., has been entirely rewritten, as has the chapter on the indicators. Changes in Part V, the section on special methods, are too many to enumerate. The book has been improved mechanically by the use of better paper, slightly larger type and the transfer of reference notes from the body of the text to the foot of the page. The index has been revised and more logically arranged. A table of volumetric factors with their logarithms has been added.

R. S. WILLIAMS.

LABORATORIUMSBUCH FUER DIE KALIINDUSTRIE. VON DR. L. TIETJENS, vereidigter und öffentlich angestellter Handelschemiker in Leopoldshall, Stassfurt, und DR. H. ROEMER, vereidigter und öffentlich angestellter chemischer Sachsverständiger für Kali und andere Salze in Leopoldshall, Stassfurt. Laboratoriumsbücher für die chemischen und verwandten Industrien. Band XII. Mit 8 in den Text gedruckten Abbildungen. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1910. pp. viii + 76. Price, M. 3.60.

This is No. 12 in a series of laboratory guides for the several

chemical industries, issued by Knapp, and is primarily of interest to the analyst who has to do with potash salts and fertilizers. The greater part of the work is devoted to detailed procedures for determining the ingredients in the various crude and concentrated potash salts of commerce. The methods employed are designated as the "Stassfurt Methoden." Explicit directions for taking samples and preparing reagent solutions are given. Separate chapters are devoted to the testing of the by-products of the German Potash Industry, of artificial potassium nitrate and crude potassium carbonate (potash). A descriptive list, arranged in alphabetical order, of the twenty-seven natural salts found in the German deposits is an interesting feature of the pamphlet. As an adjunct to the "Official Methods" in vogue for commercial purposes, this little pamphlet will be found useful.

J. H. THORP.

LES NOUVEAUTÉS CHIMIQUES POUR 1910. Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches Appliquées à la Science et à l'Industrie. Par CAMILLE POULENC, Docteur ès Sciences. Avec 216 figures intercalées dans le texte. Paris: Librairie J.-B. Baillière et Fils. 1910. pp. viii + 363. Price, Fr. 4.

The present volume of this annual contains the usual interesting collection of descriptions of apparatus and labor-saving devices gleaned from various scientific journals. Probably every chemist looking through this book will find something which will prove useful in his own work. C. A. R.

THE POLYTECHNIC ENGINEER. Published annually by the Undergraduates of the Polytechnic Institute of Brooklyn. Vol. X. 1910. pp. 134.

This well printed, neatly bound annual reflects great credit on its publishers. The present volume contains some twenty interesting technical and scientific articles by members of the staff and student body of the Institute. As being of special interest to chemists may be mentioned "The Investigation of Congo Blue and the Preparation of Congo White," by I. W. Fay, A. H. Tag and M. G. Hawkins; "Some Experiments on the Case-Hardening of Steel by Gases," by J. C. Olsen, J. R. Brierly and J. S. Weiffenback; "Initial Temperatures at which Oxides of Metals give up Oxygen to Reducing Gases," by I. W. Fay, A. F. Seeker, F. H. Lane and G. E. Ferguson; and "A Liquid which will Dissolve Cotton," by I. W. Fay and C. H. Lewis. C. A. R.